Quantized Ion Motion in Solution

Sir:

Since the observation by Edgell and coworkers[1] that ion motion in solution gives rise to far-infrared bands, whose frequencies are cation dependent, considerable attention has been directed to understanding the phenomena giving rise to these bands. The important questions raised include: what ion motion is quantized and what is the vibrating species, does the phenomenon give rise to Raman-active bands, and what is the extent of localization of the relevant vibrational motion?

Popov and coworkers[2] have shown from the spectra of the internal vibrational modes of the solvent molecules in ionic solutions in polar solvents that specific cation–solvent interactions occur as the far-infrared band arises. Edgell, *et. al*,[1,3] have shown that the far-infrared band arises in systems known to ion pair as shown by the direct cation–anion interaction which leads to lowered anion symmetry. Clearly it is important to search for the low-frequency ion motion bands in solutions of salts which are soluble in both polar and nonpolar solvents and in which ion aggregates and separated ions can each form as the solvent system is varied. It is also important to have independent evidence[4,5] for the species which are actually formed in solution.

Two striking results have emerged from our study of the laser Raman and far-infrared spectra of $Na^+AlBu_4^-$ (Bu = *n*-butyl), which is soluble in cyclohexane and tetrahydrofuran (THF), and of the THF-soluble $KAlBu_4$. First, two infrared bands attributable to ion motion are observed for $NaAlBu_4$ in cyclohexane, at 195 ± 5 and 160 ± 5 cm^{-1} as shown in Figure 1a, where as only one at *ca.* 200 cm^{-1} was anticipated on the basis of previous work.[1-3] The relative intensities of these two bands are concentration dependent, which indicates the existence of two environments for the Na^+ ion. These two ion aggregates create significantly different force fields for the cation.

The second result, of even greater interest, is the observation of a Raman band due to ion motion at 202 ± 3 cm^{-1} for $NaAlBu_4$ in cyclohexane, shown in Figure 2a. No such band is observed in the spectrum of this salt in THF.

The far-infrared spectra of THF solutions of both the Na^+ and K^+ salts of $AlBu_4^-$ in the region 140–350 cm^{-1}, shown in Figure 1b, contain a band which shifts from 195 ± 5 cm^{-1} for the Na^+ salt to 150 ± 5 cm^{-1} for the K^+ salt in addition to the anion band at 320 cm^{-1}. Figure 1b shows the change in intensity of the 195-cm^{-1} band for $NaAlBu_4$ in THF as a function of concentration in the 0.10–0.50 *M* region. It is in this region that the equivalent conductance decreases with increasing concentration as aggregation occurs.

When THF is added to 0.02 *M* solutions of $NaAlBu_4$ in cyclohexane to produce solutions with THF:salt

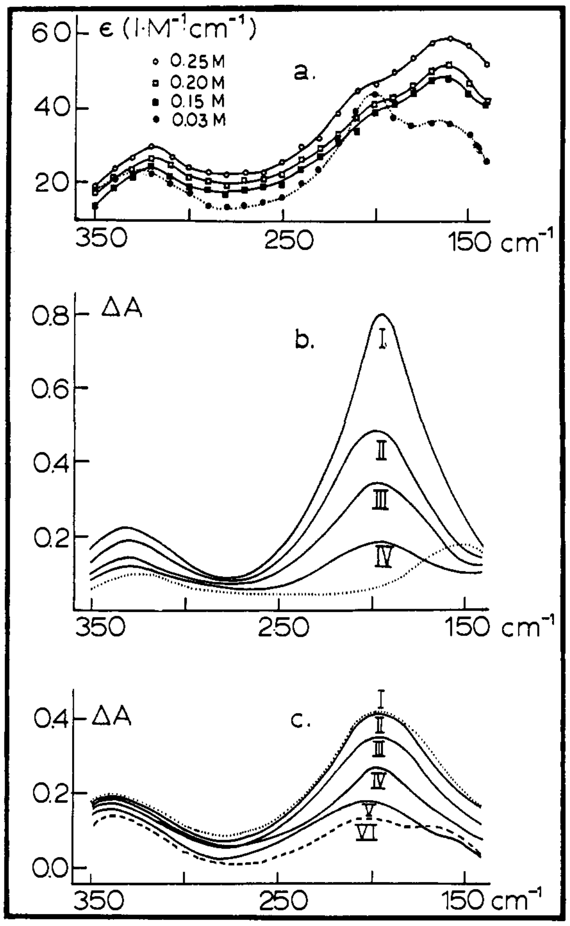

Figure 1. Infrared spectra (140–350 cm^{-1}) (Beckman IR11 spectrometer): (a) $NaAlBu_4$ in C_6H_{12}; (b) ———, $NaAlBu_4$ in THF (I, 0.5 *M;* II, 0.3 *M;* III, 0.2 *M;* IV, 0.1 *M);* · · · ·, $KAlBu_4$ in THF (0.35-mm path length); (c) 0.02 *M* $NaAlBu_4$ in C_6H_{12} (4-mm path length). *R* = mole ratio THF:Na^+ (I, *R* = 5.0; II, *R* = 4.0; III, *R* = 2.0; IV, = 1.2; V, *R* = 0.8; VI, *R* = 0.3). Solvent and cell absorption have been subtracted.

mole ratios of 0.3–5.0, the infrared spectra shown in Figure 1c are observed. Note that the band at 160 cm^{-1} vanishes as the mole ratio of THF:salt exceeds 1, while the 200-cm^{-1} band absorbance increases up to a mole ratio of 1:4. Thereafter, for increasing ratios of THF to Na^+, the intensity of this band remains constant. The change in the environment of the cation as THF is added to the $NaAlBu_4$ solutions is known from the nmr and conductivity data of Day and coworkers[5] and interpreted by us as that responsible for the change in the far-infrared spectrum.

Addition of THF to the same cyclohexane solution whose Raman spectrum is shown in Figure 2a did not significantly affect the 202-cm^{-1} band up to a mole ratio of THF:salt of 5:1, but increasing this ratio to 20:1 causes the band to disappear. Note, however, that the anion Raman bands, indicated by arrows in Figure 2, are still observed for both this THF:salt::20:1 cyclohexane solution and the solution of the salt in pure THF, although the 202-cm^{-1} band is missing. Solutions of both the Na^+ and K^+ salts in THF showed no bands below 240 cm^{-1} (Figure 2b) but did exhibit anion bands at higher frequency. Edgell, *et al.*,[3] have carefully measured the Raman spectra for a number of salts in THF including $NaCo(CO)_4$ and LiCl. Although these solutions exhibit infrared absorbance due to ion motion, no Raman

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(1) W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

(2) (a) B. W. Maxey and A. I. Popov, *ibid.*, **89**, 2230 (1967); (b) *ibid.*, **90**, 4470 (1968); (c) *ibid.*, **91**, 20 (1969); (d) J. L. Wuepper and A. I. Popov, *ibid.*, **91**, 4352 (1969).

(3) W. F. Edgell, J. Lyford, IV, R. Wright, W. M. Risen, Jr., and A. T. Watts, *ibid.*, in press.

(4) E. S. Gore and H. S. Gutowsky, *J. Phys. Chem.*, **73**, 2515 (1969).

(5) (a) E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, **90**, 503 (1968); (b) C. N. Hammonds and M. C. Day, *J. Phys. Chem.*, **73**, 1151 (1969).

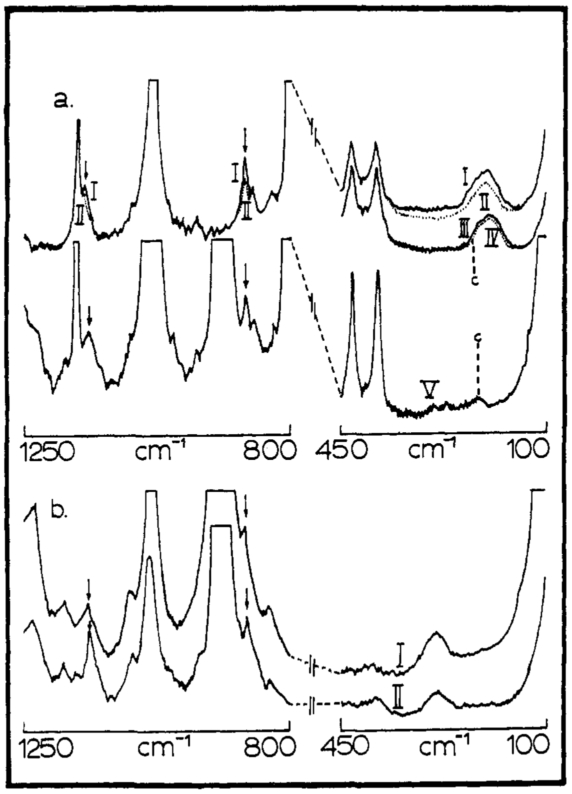

Figure 2. Laser raman spectra (Jarrell Ash 25-300 spectrometer): (a) $NaAlBu_4$ in C_6H_{12}; M = molarity in C_6H_{12}; R = mole ratio THF:Na^+ (I, 0.3 M, R = 0; II, 0.25 M, R = 0; III, 0.3 M, R = 0.5; IV, 0.3 M, R = 5.0; V, 0.20 M, R = 20.0); c = cyclohexane band. (b) I, $NaAlBu_4$ in THF; II, $KAlBu_4$ in THF. Arrows indicate bands due to vibrations of the anion.

bands were observed for them. Our experiments exclude the possibility of the Raman band being due to an impurity, and we have observed it with both 632.8- (He-Ne laser) and 514.5-nm (Ar^+ ion laser) radiation. However, they do not conclusively eliminate the possibility that an inactive anion or solvent mode is being perturbed into activity or split. This is unlikely in light of the T_d selection rules for AX_4, and selection rules for the connected *n*-butyl groups. A cyclohexane band at 240 cm^{-1} in both ir and Raman has been assigned[6] to E_u (ν_{32}, ir allowed, Raman forbidden) and is found unperturbed in our spectra. Attempts to dissolve sufficient $KAlBu_4$ in cyclohexane at room temperature have been unsuccessful.

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(6) L. Bernard, *J. Chim. Phys.*, **63**, 772 (1966).
(7) Author to whom correspondence should be addressed.

Andreas T. Tsatsas, William M. Risen, Jr.[7]
Department of Chemistry, Brown University
Providence, Rhode Island 02912
Received December 4, 1969

A Trigonal Boron Cation

Sir:

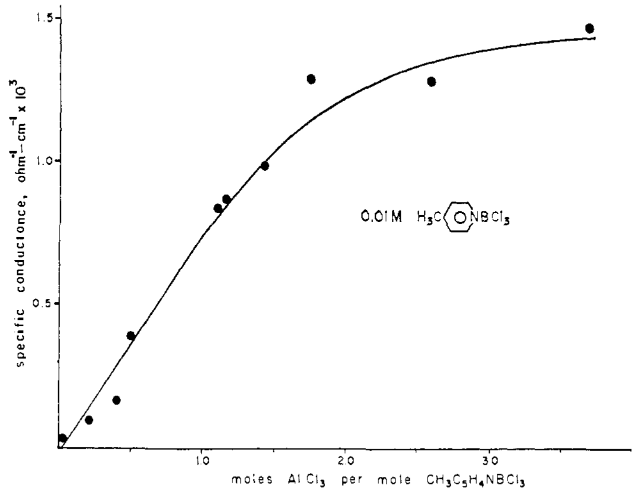
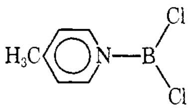


Figure 1. Conductance of 4-$CH_3C_5H_4NBCl_3$–$AlCl_3$ in CH_2Cl_2.

We wish to report direct evidence concerning the existence of a boron cation, **I**, to our knowledge the first example of a positively charged boron species with coordination number 3 which is isoelectronic to a carbonium ion. The closest reported analog to this species, $(C_6H_5)_2B^+$ solvated with ethyl methyl ketone,[1] is apparently four-coordinate.[2]



I

Although aluminum chloride does not dissolve readily in methylene chloride, a mixture of aluminum chloride and 4-methylpyridine–trichloroborane is easily soluble. The 60-MHz proton nmr spectrum of such a solution is drastically different from one of pure 4-methylpyridine–trichloroborane in methylene chloride. The neutral borane shows a sharply defined multiplet centered at τ 0.95, which has been demonstrated to consist of a doublet of two overlapping quartets arising from spin–spin coupling of the 2,6 protons on the pyridine ring to the 3,5 ring protons and to ^{11}B in the tetrahedral environment of the coordinated BCl_3 group.[3] In the presence of aluminum chloride the quartet splitting pattern completely disappears so that only the H-H doublet remains. The position of the absorption of the 2,6 hydrogens is shifted downfield relative to the tetrahedral adduct, as is the doublet arising from the 3,5 hydrogens and the singlet corresponding to the methyl substituent on the ring. The extent of this shift increases with the proportion of aluminum chloride in the sample. Representative data are given in Table I.

The collapse of the coupling pattern implies that a rapid reaction is taking place at the boron atom which decreases the symmetry of the electric field gradient at that nucleus. The concentration dependence of the chemical shifts suggest that this reaction is reversible, and the downfield direction of the shifts suggests that a positive charge is developed in the species.[4] The simplest hypothesis explaining these data is the formation of a trigonal cation derived by reversible chloride abstraction from the neutral adduct.

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