

## Infrared spectra of cyclopentadienyl-alkali metal (Li, Na) ion pairs in tetrahydrofuran and hexamethylphosphoric triamide

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### Abstract

Infrared spectra ( $4000\text{--}50\text{ cm}^{-1}$ ) of lithium and sodium cyclopentadienide solutions in tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) at various concentrations have been studied. The spectra of their THF solutions showed four fundamental vibrations of the cyclopentadienyl (Cp) anion of the contact ion pair ( $\text{Cp}^-$ ,  $\text{M}^+$ ). The effect of concentration on the spectra of CpLi and CpNa THF solution was investigated and was found to manifest itself in the ranges for out-of-plane  $\rho(\text{CH})$  bending modes,  $\nu(\text{CH})$ , and interior stretching bands. The dependence on concentration is accounted for by the presence of an equilibrium between the monomer contact ion-pair and its aggregates. Two bands of fundamental vibrations of cyclopentadienyl anion at  $686$  and at  $3045\text{ cm}^{-1}$  in the solvent-separated ion pair ( $\text{Cp}^- \parallel \text{M}^+$ ) have been estimated in the case of HMPA solutions. The broad bands in the far-infrared spectra of the THF solutions are assigned to the cation-to-anion stretching vibrations of the contact ion pair and its aggregates. The far-infrared absorption bands of the spectra of HMPA solutions are assigned to the vibrations of alkali metal cations in a solvent cage of HMPA molecules.

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### Introduction

This work is an extension of our investigation of vibrational spectra of alkali metal cyclopentadienides. Recently, we studied the IR and Raman spectra of solid CpM ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) and the Raman spectra of CpLi and CpNa solutions in THF [1]. It was found that the metal–ring bond in these compounds was predominantly ionic. An increase in the metal–Cp-ring bond polarity on going from crystal to THF solution has been found, which is due to the formation of ion pairs [1].

The ion pairs in CpM (M = Li, Na) solutions were studied by  $^7\text{Li}$  [2],  $^{13}\text{C}$  [10] and  $^1\text{H}$  [6] as well as by  $^{19}\text{F}$  (for the *p*-fluorophenyl derivatives) [3] NMR spectroscopy. Electronic absorption spectroscopy failed to provide ample information for studying the ionic states in cyclopentadienylalkali metal solutions, as they absorb below 210 nm [6]. NMR spectroscopy has shown that alkali metal cyclopentadienides in etherial solvents, THF and acetonitrile exist predominantly as contact ion pairs ( $\text{Cp}^-, \text{M}^+$ ), while in HMPA solutions, they form solvent-separated ion pairs ( $\text{Cp}^- \parallel \text{M}^+$ ) [2,3,10]. The concentration effects on the chemical shifts in PMR spectra of CpLi and CpNa in THF for concentrations 0.01–1.0 *M* observed [6], are probably due to the changes in their aggregation states, perhaps contact/solvent-separated ion pair equilibria.

In light of this, a detailed study of the ion states in the alkali metal cyclopentadienide solutions, was undertaken. We recorded the IR, including far-infrared spectra of  $\text{C}_5\text{H}_5\text{Li}$  and  $\text{C}_5\text{H}_5\text{Na}$  in THF and HMPA solutions. The vibrational spectral data on CpLi and CpNa solutions in HMPA are of special interest in view of the possibility of obtaining vibrational frequencies of the "free" cyclopentadienyl anion. IR spectra of these compounds in THF solutions in the 4000–600  $\text{cm}^{-1}$  region are reported [6], without detailed analysis of the spectra.

## Experimental

Synthesis of the alkali metal cyclopentadienides has been described previously [1]. THF was purified by conventional methods and was stored over sodium benzophenone ketyl under vacuum. THF was distilled in vacuum directly into the solution ampoules. HMPA was purified and stored over molecular sieves (4 Å) under argon or vacuum until required. All additional manipulations with solvents, solutions and cells were carried out in a specially constructed vacuum-tight drybox in a high-purity argon atmosphere. For the dilution experiments, we started with saturated solutions  $\sim 1.4 \text{ M}$  [6].

The IR spectra (4000–50  $\text{cm}^{-1}$ ) were recorded with an infrared Fourier transform spectrometer (Bruker IFS-113 v). A 256 scan data accumulation was carried out with a resolution of 2  $\text{cm}^{-1}$  for all the spectra. The solvent absorption was subtracted from each spectrum. In the region of 4000–400  $\text{cm}^{-1}$  cells of 0.02–0.12 mm thickness with KBr windows were employed, while in the region 700–50  $\text{cm}^{-1}$  cells of 0.2–1.0 mm thickness with polyethylene windows, made in this laboratory, were used. The Raman spectra of solutions contained in sealed glass ampoules were measured with a Ramanor-HG-2S spectrometer equipped with a Spectra-Physics 164  $\text{Ar}^+$  laser ( $\lambda$  5145 Å, *P*  $\sim$  100 mW).

## Results and discussion

### *Cyclopentadienyl anion vibration region*

The IR spectral data of CpLi and CpNa solutions in THF and HMPA with frequency assignments are given in Table 1. Four fundamental vibrations, allowed in the IR spectrum for  $D_{5h}$  symmetry of  $\text{C}_5\text{H}_5^-$  anion, are observed in the spectra of the THF solutions. In addition, weak broad bands of transitions of the second order (overtones and combinations) are seen in the region above 1500  $\text{cm}^{-1}$ . In the spectra of CpLi solutions in THF, a weak band at 1340  $\text{cm}^{-1}$  of the transition,

Table 1

IR spectra for solutions of CpLi and CpNa in THF and HMPA (Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad.)

THF		Assignment for symmetry $C_{5v}$ of $(Cp^-, M^+)$	HMPA		Assignment for symmetry $D_{5h}$ of $\eta^o-C_5H_5^-$
$C_5H_5Li$	$C_5H_5Na$		$C_5H_5Li$	$C_5H_5Na$	
322		<sup>a</sup>			
370	152?	<sup>a</sup>			
426m	196m	$\nu_4, A_1, \nu(M-Cp)$	395m	202m	$\nu(M^+ \cdots S_n)$
508br	232	<sup>a</sup>	508m		
712		<sup>a</sup>			
723		<sup>a</sup>			
732vs	705vs	$\nu_3, A_1, \rho(CH)$	686vs	688vs	$\nu_4, A'_2, \rho(CH)$
755	724	<sup>a</sup>			
1009s	1006s	$\nu_8, E_1, \beta(CH)$			
1340vw		$\nu_{12}, E_2, \nu(CC)$			
1432m	1431m	$\nu_7, E_1, \nu(CC)$	<sup>b</sup>	<sup>b</sup>	
1554w,br	1539w,br	$\nu_3 + \nu_{14}$			
	1669vw,br				
3070m	3058m	$\nu_5, E_1, \nu(CH)$	3044m	3045m	$\nu_5, E'_1, \nu(CH)$
	3066	<sup>a</sup>			

<sup>a</sup> Ion pair aggregate bands; see text. <sup>b</sup> Strong absorption region of HMPA.

forbidden in the IR spectrum for  $D_{5h}$  symmetry of  $C_5H_5^-$  anion, but allowed for  $C_{5v}$  symmetry, appeared. We found that the spectral pattern depended on the solution concentration, which is very pronounced in the region of the  $\rho(CH)$  out-of-plane bending mode and also for the bands of  $\nu(CH)$  stretching vibrations. The most intense band of  $\rho(CH)$  vibrations exhibits a complex structure in the spectra of concentrated solutions. The band profile observed is overlapped by at least two bands from CpNa and four bands from CpLi (Figs. 1, 2). The related intensities of the components depend on the concentration of the solutions. Dilution of CpNa solution (Fig. 1) leads to a decrease in the intensity of the high-frequency band relative to that of the low-frequency band. In the highly diluted solutions only the band at  $705\text{ cm}^{-1}$  remains. As the CpLi solution is being diluted (Fig. 2), we observe first the disappearance of the high-frequency wing, then the disappearance of the low-frequency shoulders of the central band at  $732\text{ cm}^{-1}$ . The concentration dependence is also observed for the  $\nu(CH)$  band in the spectra of CpNa solutions in THF (Fig. 3). In the spectrum of the concentrated solution the  $\nu(CH)$  band has a weakly-pronounced shoulder at  $3066\text{ cm}^{-1}$  on the high-frequency side. As the solution is being diluted, a shift of the band maximum in the low-frequency range takes place and a symmetric contour band at  $3058\text{ cm}^{-1}$  is observed in the spectrum of the diluted solution. The spectra of the diluted CpLi and CpNa solutions in THF are, in the main, in agreement with those obtained by Ford [6], indicating only one  $\rho(CH)$  frequency value. It should be noted that in the spectrum of CpNa measured by Ford [6] there is a band at  $1380\text{ cm}^{-1}$ , which was not present in one spectra.

It is known [1,7] that the frequency of  $\rho(CH)$  mode in the IR spectra of cyclopentadienyl complexes is most sensitive to the metal–ring bond polarity and so decreases with increasing metal–ring bond polarity. Thus, the decrease in the frequency of the  $\rho(CH)$  mode upon transition from the spectrum of CpLi solution

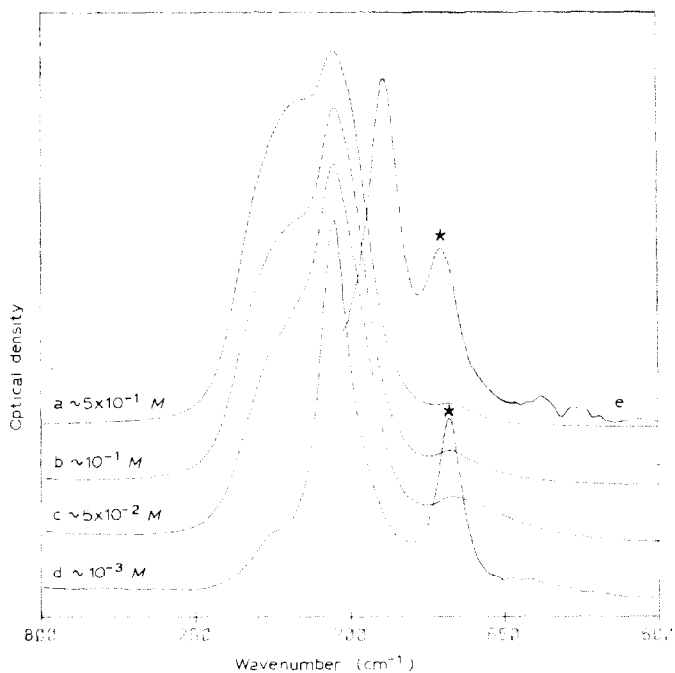


Fig. 1. IR spectra of  $C_5H_5Na$  in THF solution (a-d) and in HMPA solution (e) in the  $\rho(CH)$  vibration region. \* Cyclopentadiene (decomposition product) band at  $668 cm^{-1}$  arises after exposure to a portion of air in the drybox.

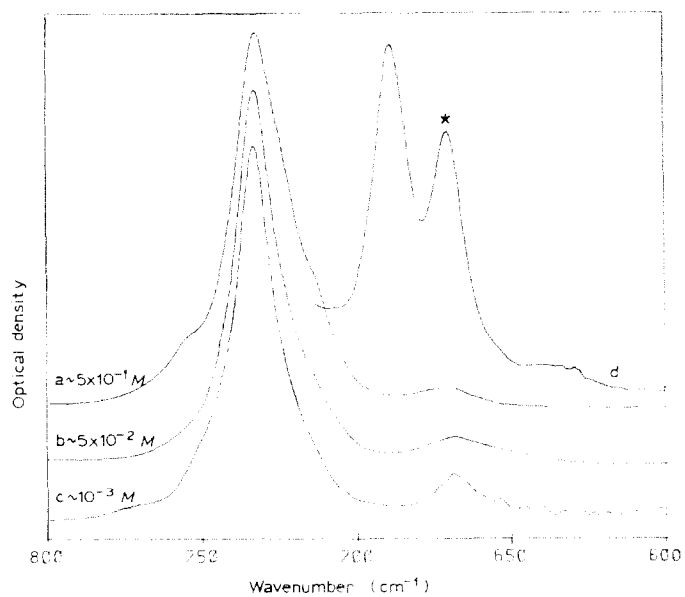


Fig. 2. IR spectra of  $C_5H_5Li$  in THF solution (a-c) and in HMPA solution (d) in the  $\rho(CH)$  vibration region. \* see Fig. 1.

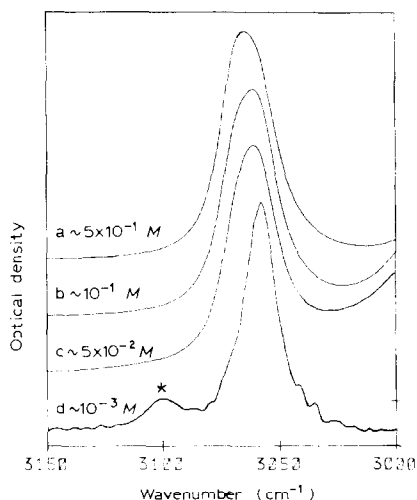


Fig. 3. IR spectra of  $C_5H_5Na$  in THF solution in the  $\nu(CH)$  vibration region. \* Cyclopentadiene band at  $3105\text{ cm}^{-1}$ .

in THF to the spectrum of the CpNa solution corresponds to an increase in the polarity of the metal–cyclopentadienyl ring bond and supports the formation of the contact ion pairs in THF.

The observed concentration dependence of the spectra of THF solutions is consistent with the fact that there is an equilibrium in solution between the contact ion pairs and its aggregates. The aggregation of carbanion alkali metal salts in solvents with low dielectric constants was determined by different physical methods, with EPR spectroscopy being the most informative. Different aspects of the process of formation of ion pair aggregates in solutions were studied by EPR spectroscopy, and their structures deduced [8,9]. Our data did not allow us to arrive at a definite conclusion on the structure of aggregates in THF solutions, however we may assume that CpLi forms different types of aggregates, whereas CpNa forms only one, which was confirmed by their far-infrared spectra (see below). Aggregates were found to be present down to concentrations of  $10^{-3}\text{ M}$ .

Moving from solutions of CpLi and CpNa in THF to solutions of the same in HMPA, the frequency of the  $\rho(CH)$  band shifts to the low-frequency region up to  $686\text{ cm}^{-1}$  (Figs. 1, 2) and its value is practically independent of cation, and solution concentration. The NMR  $^{13}C$  chemical shifts and spin–spin coupling constants  $^1J(^{13}C-H)$  for CpLi and CpNa [10] as well as the NMR  $^{19}F$  chemical shifts for their *p*-fluorophenyl derivatives [3] in HMPA coincide well. All the above-mentioned data are evidence for the formation of solvent-separated ion pairs of “free” solvate ions, as the spectral characteristics of these species are practically alike. Thus, the cyclopentadienyl ring in cyclopentadienide lithium and sodium in HMPA solutions are in the same form and are closer to the “free” anion state. Unfortunately, we failed to obtain a full spectrum of the active infrared vibrations for the cyclopentadienyl anion in HMPA, because of strong solvent absorption. Besides the  $\rho(CH)$  band, we observed a  $\nu(CH)$  vibration band at  $3045\text{ cm}^{-1}$ . We attempted to measure the Raman spectrum of the CpLi and CpNa solutions in HMPA, but with the

exception of the most intense line of the ring breathing mode at  $1122\text{ cm}^{-1}$ , the spectrum was not very well resolved because of strong fluorescence induced by the laser beam.

Recently [11] the structure of a crystalline compound consisting of cation  $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+$  and anion  $\text{C}_5\text{H}_5^-$  was determined by X-ray crystallography. IR frequencies for the “free”  $\eta^0\text{-C}_5\text{H}_5$  anion:  $3045\text{ }\nu(\text{CH})$ ,  $1000\text{ }\beta(\text{CH})$  and shoulder at  $673\text{ cm}^{-1}\text{ }\rho(\text{CH})$ , which are close to the data obtained by us for HMPA solutions were reported [11]. Thus, the transition from a cation-bonded cyclopentadienyl anion in THF solutions to the “free” anion is accompanied by a decrease in the  $\rho(\text{CH})$  and  $\nu(\text{CH})$  frequencies. The lowest values of  $\rho(\text{CH})$  and  $\nu(\text{CH})$  frequencies recorded by Fritz [12] in the IR spectrum of solid cesium cyclopentadienide were  $668$  and  $3021\text{ cm}^{-1}$ . However, the frequency at  $668\text{ cm}^{-1}$  is consistent with that of the decomposition product band of cyclopentadiene  $\text{C}_5\text{H}_6$  observed, as a rule, in the spectra of the alkali metal cyclopentadienides [1,12]. The value of the  $\nu(\text{CH})$  frequency in the spectra of the solid CpM (M = Li, Na, K) measured by Fritz [12] is  $30\text{--}40\text{ cm}^{-1}$  below that of the  $\nu(\text{CH})$  frequency in the spectra of these compounds recorded by us [1]. Thus, the value of the  $\nu(\text{CH})$  at  $3021\text{ cm}^{-1}$  in the spectrum of CpCs appears to be incorrect.

#### *Far-infrared spectra (FIR)*

In a previous paper [1] we reported some weak lines in the low frequency region ( $150\text{--}130\text{ cm}^{-1}$ ) of Raman spectra of CpLi and CpNa solutions in THF. Those lines were assigned to the tilt mode  $\nu^{\text{tilt}}(\text{M-Cp})$  of the anions in the contact ion pairs ( $\text{Cp}^-, \text{M}^+$ ). It was also shown that the inter-ion  $\nu(\text{M-Cp})$  stretching mode does not appear in the Raman spectra, owing to its low intensity, which is related to the high degree of  $\text{Cp}^-\text{-M}^+$  bond polarity. The stretching inter-ion mode must appear in the IR spectra of contact ion pairs. Thus, the broad band of the stretching inter-ion mode was observed in the FIR spectra of alkali-naphthalene [13] and alkanthracene [14] ion pairs in THF solutions.

The FIR spectra of CpLi and CpNa solutions in THF and HMPA are given in Table 1. The effects of concentration on the spectra are shown in Figs. 4 and 5. A broad band with an asymmetric contour and maximum at  $232\text{ cm}^{-1}$  (Fig. 4) is observed in the spectrum of a saturated solution of CpNa. As the solution is diluted, a second maximum, of which the relative intensity increases, appears at low-frequency. Two maxima of approximately equal intensities at  $232$  and  $196\text{ cm}^{-1}$  are clearly resolved on the band in the spectrum of the diluted solution. In the spectrum of the saturated CpLi solution one observes a more complicated pattern (Fig. 5), resembling the spectrum of solid CpLi in Nujol [1]. A broad band with maxima at  $508$ ,  $426$ ,  $370$  and  $322\text{ cm}^{-1}$  was observed in the spectrum, the band at  $508\text{ cm}^{-1}$  being of a complex nature with unclearly resolved submaxima. As the solution is diluted, the intensity of the band at  $508\text{ cm}^{-1}$  decreases, while the low-frequency maxima increase relative to the central maximum at  $426\text{ cm}^{-1}$ . With further dilution, the intensity of low-frequency maxima also decrease. A small shift of the band maxima is observed with dilution. The spectral pattern seems to conform to the complicated character of the equilibria, which involves participation of different types of aggregates which occur in the CpLi solution in THF. The lowest concentration limit, at which spectra with an acceptable signal-to-noise ratio can be recorded, is determined by the band intensity and solvent background. We failed to obtain the

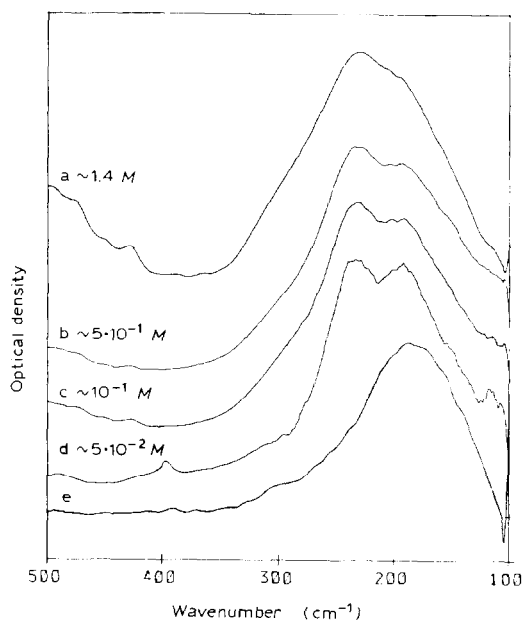


Fig. 4. FIR spectra of  $C_5H_5Na$  (a-d) and  $NaI$  (e) in THF solution.

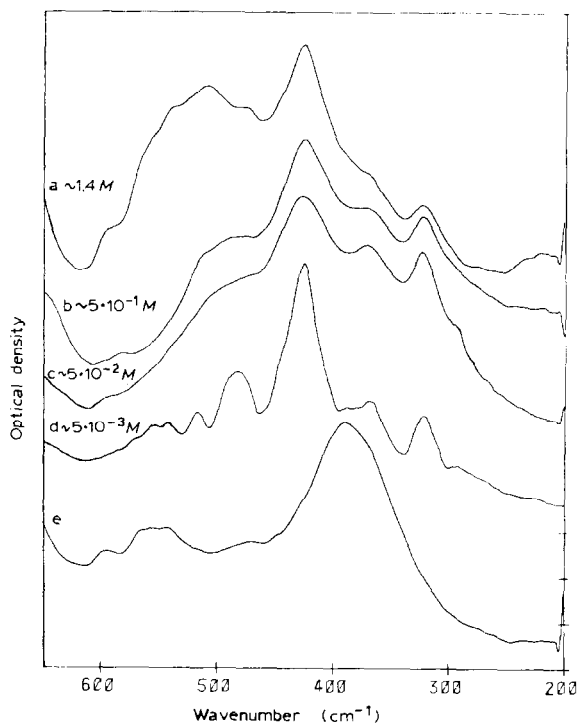


Fig. 5. FIR spectra of  $C_5H_5Li$  (a-d) and  $LiCl$  (e) in THF solution.

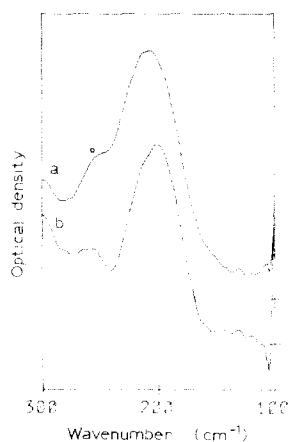


Fig. 6. FIR spectra of  $C_5H_5Na$  (a) and  $NaI$  (b) in HMPA solution. <sup>o</sup> see Fig. 7.

spectrum of the THF solutions diluted more than 30-fold for  $CpNa$  and 300-fold for  $CpLi$  relative to saturated solution, neither was a complete picture of the change in the spectrum with dilution obtained. It was found to be related to the conditions under which the FIR spectra were recorded and to the relative weakness of the bands. In accordance with the tendency for the intensity of the bands to change with dilution, we believe that the bands at  $196$  and  $426\text{ cm}^{-1}$  can be assigned to the stretching interior  $\nu(M-Cp)$  mode of the contact ion pair ( $Cp^-, Na^+$ ) and ( $Cp^-, Li^+$ ) respectively. The rest of the bands are probably due to the presence of ion pair aggregates.

The spectra of  $CpLi$  and  $CpNa$  become much simpler when HMPA solutions are used (Figs. 6 and 7). A band at  $202\text{ cm}^{-1}$  is observed in the spectrum of  $CpNa$  in solutions of HMPA, whereas two bands of about equal intensities at  $395$  and  $508\text{ cm}^{-1}$  are observed in the spectra of  $CpLi$  in HMPA solutions. The spectra are consistent with the spectra of simple lithium and sodium salts in HMPA solutions obtained by us (Table 2). Table 2 also lists spectral data on  $LiCl$  and  $NaI$  solutions in THF, which are in agreement with those found in the literature [4,15]. Exact coincidence of the FIR spectra of the lithium and the sodium salts with such varied anions as halide-anion and cyclopentadienyl-anion is additional evidence for the formation of solvent-separated ion-pairs or "free" solvated ions in HMPA solutions. The band observed in the spectra may be assigned to the vibrations of lithium or sodium cation in a solvent cage of HMPA molecules.

The presence of two bands in the spectra of lithium salt solutions in HMPA was an unexpected event. A study of the literature data has shown that the spectra of alkali metal salts in solvents with a strong solvating power, where they form solvent-separated ion-pairs, show a broad band, which is essentially independent of the anion and solvent. The band corresponds to the triple degenerate vibration in the tetrahedral or octahedral primary solvation shell [17]. Thus, one band at  $430-440$  [5] and another band  $195-205\text{ cm}^{-1}$  [4] are observed in the spectra of lithium and sodium salts in DMSO solutions respectively. The presence of two bands in the spectra of lithium salt solutions in HMPA may be due to distortion of the tetrahedral environment (the solvation number is equal to four for HMPA [16])



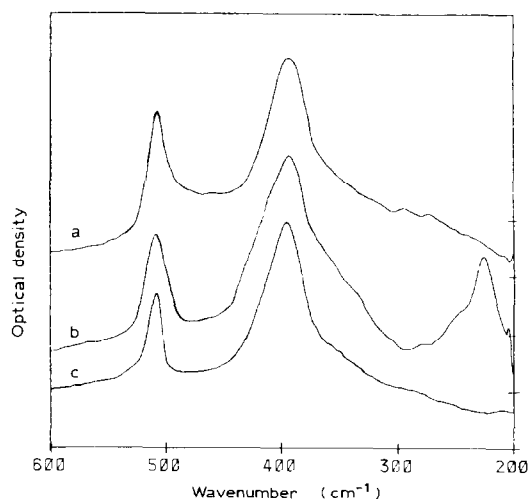


Fig. 7. FIR spectra of HMPA solutions of  $C_5H_5Li$  (a),  $LiCl$  (b) and  $LiI$  (c). The intense HMPA bands at 482s, 377m, 350m, 295m, 245w have been subtracted.

Table 2

FIR spectra of  $LiCl$ ,  $LiI$  and  $NaI$  solutions

salt	THF	HMPA
$LiCl$	368sh, 388	226 <sup>a</sup> , 395, 508
$LiI$		395, 508
$NaI$	189	201

<sup>a</sup> The origin of the 226  $cm^{-1}$  band is unclear.

of lithium cation because of steric hindrance arising from solvation of a small lithium cation by the much bulkier HMPA molecules. The band at 508  $cm^{-1}$  may also be related to high-frequency shift of the HMPA band at 482  $cm^{-1}$  as a result of solvent interactions with cations, which is maximal in the case of  $Li^+$ , relative to  $Na^+$  and  $K^+$  cations. We think this result requires further investigation.

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