The IR spectra of alkaline and alkaline earth metal perchlorate and of lithium bromide solutions in acetonitrile, obtained with the help of FTIR measurements in the region of the C-N stretching mode of the solvent, reveal bands produced by acetonitrile molecules in the solvation shells and bands of ClO$_4^-$ ions in contact and solvent separated ion pairs. The shift and the attenuation of the C-N stretching band of acetonitrile at 2254 cm$^{-1}$ is used for the calculation of cation solvation numbers for Li$^+(4)$, Na$^+(4)$, Mg$^{2+}(6)$, Ca$^{2+}(6)$ and Ba$^{2+}(6)$. No solvation is assumed for the contact ion pairs of LiClO$_4$, LiBr, NaClO$_4$, Mg(ClO$_4$)$_2$, Ca(ClO$_4$)$_2$, and Ba(ClO$_4$)$_2$. The association constants of the symmetrical electrolytes are compared to those obtained from other methods.
FTIR Spectroscopy of Ion Solvation of LiClO₄ and LiSCN in Acetonitrile, Benzonitrile, and Propylene Carbonate

J. Barthel,* R. Buchner, and E. Wismeth

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FTIR spectra of lithium perchlorate and lithium thiocyanate in acetonitrile, benzonitrile, and propylene carbonate were recorded in the temperature range from 5 to 45°C. New bands due to solvent molecules in the primary solvation shell of the lithium ions were detected in the region of the CN stretching mode of the nitriles and of the CO stretching mode of propylene carbonate. The band structures were studied in detail by deconvolution with band-fitting procedures and mean cation solvation numbers were deduced from the band area of the bulk solvent. For the systems acetonitrile–lithium perchlorate, benzonitrile–lithium perchlorate, and benzonitrile–lithium thiocyanate, solvation numbers of “free” and “bound” lithium ions were calculated with the help of the degree of association obtained from suitable anion vibrations.

KEY WORDS: FTIR spectroscopy; ion solvation; ion association; dipolar aprotic solvents.
Experiments

Nicolet 60 SX FT-IR (Ge/KBr beam splitter with DTGS detector)

Transmission geometry

\( \text{BaF}_2 \) window
12.5 um Tin spacer (BN - Benzonitrile)
21.0 um Lead spacer (AN - Acetonitrile)

16.0 um (1994 salt dependence paper)

1 bounce ZnSe ATR (PC – Propylene Carbonate)

Single bounce ZnSe ATR

AN refluxed with CaH2 in dry N2
( water < 15 ppm, Organic impurities < 20 ppm)

BN stored with 0.4 nm molecular sieve
( water < 10 ppm, organic impurity < 500 ppm)
**IR Spectra of Acetonitrile / LiClO₄**

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>AN/LiClO₄</th>
<th>AN/LiSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (ion)</td>
<td>((v_3 + v_4)^{\text{shift}})</td>
<td>2306.3</td>
<td>2304.9</td>
</tr>
<tr>
<td>2</td>
<td>((v_3 + v_4))</td>
<td>2293.1</td>
<td>2292.9</td>
</tr>
<tr>
<td>3 (ion)</td>
<td>(v_2^{\text{shift}})</td>
<td>2275.5</td>
<td>2274.0</td>
</tr>
<tr>
<td>4</td>
<td>(v_2)</td>
<td>2253.5</td>
<td>2253.5</td>
</tr>
<tr>
<td>5</td>
<td>(v_2^{\text{hot}})</td>
<td>2249.1</td>
<td>2249.2</td>
</tr>
</tbody>
</table>

\(v_2\): CN-stretch  
\(v_3\): CH₃ s-deform (1385 cm\(^{-1}\))  
\(v_4\): CC stretch (920 cm\(^{-1}\))  

**Hot**:

- Hot band (transition between excited state)  
- \(N/N_0 \sim e^{-E/kT}\)
IR Spectra of Acetonitrile / LiClO$_4$

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>AN/LiClO$_4$</th>
<th>AN/LiSCN</th>
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<tbody>
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<td>1 (ion)</td>
<td>$(v_3 + v_4)^{\text{shift}}$</td>
<td>2306.3</td>
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<td>$v_2^{\text{shift}}$</td>
<td>2275.5</td>
<td>2274.0</td>
</tr>
<tr>
<td>4</td>
<td>$v_2$</td>
<td>2253.5</td>
<td>2253.5</td>
</tr>
<tr>
<td>5</td>
<td>$v_2^{\text{hot}}$</td>
<td>2249.1</td>
<td>2249.2</td>
</tr>
</tbody>
</table>
Salt dependence of $\Delta \nu_{\text{CN}} = \Delta \nu_{\text{CN}}^{\text{shift}} - \Delta \nu_{\text{CN}}$

$\Delta \nu_{\text{CN}}$

$\varphi = \frac{e}{A^{-2}}$

1. NaClO$_4$
2. Ba(ClO$_4$)$_2$
3. Sr(ClO$_4$)$_2$
4. Ca(ClO$_4$)$_2$
5. LiClO$_4$
IR Spectra of LiClO$_4$ anion

Free ClO$_4^-$: 1102 cm$^{-1}$
(tetrahedral T$_D$ symmetry)

(b) Combination of $\nu_2 + \nu_4$

Antisymmetric Cl-O deformation
(C$_{3v}$ symmetry)
(1) 1134 cm$^{-1}$: Contact Ion Pair
(2) 1124 cm$^{-1}$: Solvent Separated IP

(1') 1068 cm$^{-1}$: CIP
(It might be $\nu_1$ stretch)
IR Spectra of Ca(ClO$_4$)$_2$ anion

Antisymmetric Cl-O deformation (C$_{3v}$ symmetry)
(1) 1166 cm$^{-1}$ : Contact Ion Pair
(2) 1141 cm$^{-1}$ : Solvent Separated IP
(3) 1124 cm$^{-1}$ : Solvent Separated IP

Ca$_2^+$ ⋅ ⋅ ⋅ AN ⋅ ⋅ ⋅ ClO$_4^-$

Band (3) is shown for Ca(ClO$_4$)$_2$ and Ba(ClO$_4$)$_2$
Cation Solvation Number

\[ c_0 = c_{\text{solv}} + c_{\text{SIP1}} \]
\[ c_{\text{solv}} = c_{\text{free}} + c_{\text{SSIP}} + c_{\text{SIP2}} \]

\( c_0 \): Concentration of ion

<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
<th>Solvated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}^+ \cdots \text{ClO}_4^- )</td>
<td>CIP(_1)</td>
<td>No</td>
</tr>
<tr>
<td>( \text{C}^+ \cdots \text{AN} \cdots \text{ClO}_4^- )</td>
<td>SSIP</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{C}^+ )</td>
<td>Free</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{ClO}_4^- \cdots \text{C}^{2+} \cdots \text{ClO}_4^- )</td>
<td>CIP(_1)</td>
<td>No</td>
</tr>
<tr>
<td>( \text{C}^{2+} \cdots \text{ClO}_4^- )</td>
<td>CIP(_2)</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{C}^{2+} \cdots \text{AN} \cdots \text{ClO}_4^- )</td>
<td>SSIP</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{C}^{2+} )</td>
<td>Free</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Cation Solvation Number

\[ c_0 = c_{\text{solv}} + c_{\text{SIP1}} \]

\[ c_{\text{solv}} = c_{\text{free}} + c_{\text{SSIP}} + c_{\text{SIP2}} \]
Cation Solvation Number

\[ c_0 = c_{\text{solv}} + c_{\text{SIP1}} \]
\[ c_{\text{solv}} = c_{\text{free}} + c_{\text{SSIP}} + c_{\text{SIP2}} \]

\[ A_{\text{CN}}^{\text{shift}} = n d \epsilon_{\text{CN}}^{\text{shift}} c_{\text{solv}} \]
\[ A_{\text{ClO}_4}^{\text{ClP1}} = n d \epsilon_{\text{ClO}_4}^{\text{ClP1}} c_{\text{ClP1}} \]

\[ A_{\text{CN}} = n \epsilon_{\text{CN}} c_{\text{AN}} \]
\[ A_{\text{CN}*} = n \epsilon_{\text{CN}*} c_{\text{AN}*} \]

\[ n : \text{cation solvation number} \]
\[ n = 4 \]

\[ \text{AN}^* : \text{CN stretching mode of AN in a sample of pure AN} \]
\[ \text{AN} : \text{AN which does not participating in solvation shell} \]
Cation Solvation Number

\[ A_{CN}^{\text{shift}} = n d \varepsilon_{CN}^{\text{shift}} c^{\text{solv}} \]

\[ A_{CN} = n \varepsilon_{CN} c_{AN} \]

\[ A_{CN}^* = n \varepsilon_{CN}^* c_{AN}^* \]

\[ \varepsilon_{CN}^{\text{shift}} = \frac{A_{CN}^{\text{shift}}}{A_{CN}^* - A_{CN}} \cdot \varepsilon_{CN} \]

n : cation solvation number

n = 4
Cation Solvation Number

\[ c_0 = c_{\text{solv}} + c_{\text{SIP1}} \]

\[ A_{\text{CN}}^{\text{shift}} = n d \varepsilon_{\text{CN}}^{\text{shift}} c_{\text{solv}} \]
\[ A_{\text{ClO}_4}^{\text{ClIP1}} = n d \varepsilon_{\text{ClO}_4}^{\text{ClIP1}} c^{\text{ClIP1}} \]

\[ c^0 = \frac{A_{\text{CN}}^{\text{shift}}}{n d \varepsilon_{\text{CN}}^{\text{shift}}} + \frac{A_{\text{ClO}_4}^{\text{ClIP1}}}{d \varepsilon_{\text{ClO}_4}^{\text{ClIP1}}} \]

\[ \varepsilon_{\text{CN}}^{\text{shift}} = \frac{A_{\text{CN}}^{\text{shift}}}{A_{\text{CN}*} - A_{\text{CN}}} \cdot \varepsilon_{\text{CN}} \]

n : cation solvation number
\[ n = 4 \]
Cation Solvation Number

\[ c_0 = c_{\text{solv}} + c_{\text{SIP1}} \]

\[ A_{\text{CN}}^{\text{shift}} = n d \varepsilon_{\text{CN}}^{\text{shift}} c_{\text{solv}} \]
\[ A_{\text{ClO}_4}^{\text{CIP1}} = n d \varepsilon_{\text{ClO}_4}^{\text{CIP1}} c_{\text{CIP1}} \]

\[ \varepsilon_{\text{CN}}^{\text{shift}} = \frac{A_{\text{CN}}^{\text{shift}}}{A_{\text{CN}}^{*} - A_{\text{CN}}} \cdot \varepsilon_{\text{CN}} \]

\[ c^0 = \frac{A_{\text{CN}}^{\text{shift}}}{n d \varepsilon_{\text{CN}}^{\text{shift}}} + \frac{A_{\text{ClO}_4}^{\text{CIP1}}}{d \varepsilon_{\text{ClO}_4}^{\text{CIP1}}} \]

\[ n : \text{cation solvation number} \]
\[ n = 4 \]

\( n \) determined by measurements at two different concentrations
Cation Solvation Number

\[ n = 4 \ (\text{Li}^+, \text{Na}^+) \]

\[ n = 6 \ (\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}) \]
Association Constants

\[ C^+ + A^- \rightleftharpoons [C^+A^-]^0 \]

\[ K_c = \frac{c^{\text{cIP}}}{(c^0 - c^{\text{cIP}})^2} \]

\[ \text{Graph: NaClO}_4 \]

\[ \text{Graph: LiBr} \]
IR Spectra of Benzonitrile/ LiClO₄

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>BN/LiClO₄</th>
<th>BN/LiSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (ion)</td>
<td>$\nu_4$CN\text{shift}</td>
<td>2254.9</td>
<td>2253.3</td>
</tr>
<tr>
<td>2</td>
<td>$\nu_4$CN\text{monomer}</td>
<td>2242.6</td>
<td>2242.0</td>
</tr>
<tr>
<td>3 (ion)</td>
<td>$\nu_4$CN\text{dimer}</td>
<td>2228.8</td>
<td>2228.8</td>
</tr>
</tbody>
</table>
IR Spectra of Benzonitrile/ LiClO$_4$

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>BN/LiClO$_4$</th>
<th>BN/LiSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (ion)</td>
<td>$\nu_4$CN$^{\text{shift}}$</td>
<td>2254.9</td>
<td>2253.3</td>
</tr>
<tr>
<td>2</td>
<td>$\nu_4$CN$^{\text{monomer}}$</td>
<td>2242.6</td>
<td>2242.0</td>
</tr>
<tr>
<td>3</td>
<td>$\nu_4$CN$^{\text{dimer}}$</td>
<td>2228.8</td>
<td>2228.8</td>
</tr>
</tbody>
</table>
IR Spectra of Propylene Carbonate / LiClO$_4$

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
<th>PC/LiClO$_4$</th>
<th>PC/LiSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (ion)</td>
<td>$\nu_1$CO$^{\text{shift}}$</td>
<td>1779.5</td>
<td>1779.4</td>
</tr>
<tr>
<td>2</td>
<td>$\nu_1$CO$^{\text{monomer}}$</td>
<td>1753.1</td>
<td>1755.9</td>
</tr>
</tbody>
</table>

![IR Spectra Diagram](image)
Mean Solvation Number

\[ 1 - \frac{E_S}{E_S^*} = \frac{c_S^* - c_S + \bar{n} \cdot c}{c_S^*} \]

\[ \frac{c_S}{c_S^*} - \frac{E_S}{E_S^*} = n \frac{c}{c_S^*} \]

\( E_S^* \): Absorbance of AN*

AN* : CN stretching mode of AN in a sample of pure AN
AN : AN which does not participating in solvation shell

**Fig. 5.** Determination of the mean solvation number, \( \bar{n} \) of LiClO₄ in AN at 25°C by linear regression of Eq. (3).
Table VI. Mean Solvation Numbers, $\bar{n}$, of the Studied Electrolytes at 25°C in the Concentration Range $c_{\text{min}} - c_{\text{max}}^{a}$

<table>
<thead>
<tr>
<th>System</th>
<th>$\bar{n}$</th>
<th>$c_{\text{min}} - c_{\text{max}}$</th>
<th>$K_A$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN/LiClO$_4$</td>
<td>3.4</td>
<td>0.05–0.73</td>
<td>22.0</td>
<td>10</td>
</tr>
<tr>
<td>AN/LiSCN</td>
<td>2.7</td>
<td>0.07–0.68</td>
<td>1775</td>
<td>10</td>
</tr>
<tr>
<td>BN/LiClO$_4$</td>
<td>2.0–1.7</td>
<td>0.11–1.00</td>
<td>224</td>
<td>10</td>
</tr>
<tr>
<td>BN/LiSCN</td>
<td>2.0–1.6</td>
<td>0.11–1.02</td>
<td>2690</td>
<td>30</td>
</tr>
<tr>
<td>PC/LiClO$_4$</td>
<td>2.3–1.7</td>
<td>0.12–1.29</td>
<td>5.20</td>
<td>11</td>
</tr>
<tr>
<td>PC/LiSCN</td>
<td>2.0–1.6</td>
<td>0.13–1.19</td>
<td>180</td>
<td>30</td>
</tr>
</tbody>
</table>
Anion spectra

(a) AN/LiClO4 0.75 M
(b) BN/LiClO4 1.02 M