

Real and imaginary parts of the vibrational correlation function extracted from the highly overlapping Raman bands of liquid electrolyte solutions

Dmitry Nerukh - Unilever Centre for Molecular Informatics, Chemistry Department, University of **Cambridge**, Lensfield Road, Cambridge, CB2 1EW, UK; dn232@cam.ac.uk; www.chem.pwf.cam.ac.uk/~dn232

The method

Basing on the theoretical considerations the **model** for the spectrum is chosen which includes:

- the set of spectral bands;
- the shape for each band.

The **experimental isotropic Raman** scattering spectra of acetonitrile and its NaI and LiBF₄ solutions at 25, 50 and 75°C are measured and corrected to the apparatus function.

The **hierarchy** of the models is built varying the complexity of the resulting spectral profile.

Using the rigorously valid fitting procedure too simple and too sophisticated models are “**filtered out**” thus deducing the **most suitable model**.

The following **requirements** are fulfilled:

- the fit is **unique**;
- the model is **complex enough** to satisfy the assumptions behind the least squares method, that is the residuals are purely random and do not include any trends due to improper theoretical profile.

The correctness of the model is checked by

- **goodness of fit;**
- the analysis of the deviations.

If the model is not complex enough to reproduce the spectrum (the deviations show a trend) the model is made more elaborate.

An original minimization algorithm [T. R. Griffiths, D. A. Nerukh, and A. Ereimenko, *Phys. Chem. Chem. Phys.*, **1**, 3199 (1999)] is used that is a variation of the evolutionary class of algorithms. It has an ability to find the **global solution**. In addition it is extremely **robust** and always finds the solution even for **high-dimensional**, very shallow profiles of the minimizing function.

The fitted solution is checked for its **uniqueness**: Several fitting runs are performed starting from substantially varying initial values of the parameters. The resulting dispersion of approximation and the values of the fitting parameters are analysed:

A histogram showing the distribution of the dispersion of approximation x_{21}^* . The x-axis is labeled 'dispersion of approximation $\times 10^4$ ' and ranges from 4.25 to 4.40. The y-axis represents frequency. Most data points are clustered between 4.25 and 4.35. Three bars at the higher end of the scale (approximately 4.37, 4.38, and 4.39) are significantly taller than the others and are labeled 'outliers' with arrows pointing to them.

The confidence intervals are calculated using the **Monte Carlo** method:

1. From the fitted profile using the experimental standard deviations a set of fictitious spectra is simulated;
2. They are fitted;
3. Statistical characteristics of the resulting parameters are calculated.

The confidence intervals of the parameters are analysed.

If some parameters are not confident the model

The model is **reformulated** (adjusted) so that

- if it is too complex: some parameters are fixed; relationships between the parameters are introduced; simpler band shapes are used;
- if it is too simple: more bands is used or their shapes are made more elaborate.

The **structural and dynamical characteristics** are obtained from the parameters of the fitted profiles

The **bands positions**, their **heights** reflect the structure of the liquid;
The **shifts** of the band centres relative to each other and to the gas-phase bands indicate the changes in intramolecular interactions.

The details of the **band shapes** are the characteristics of the intermolecular dynamics in the liquid. The vibrational autocorrelation function C is related to the isotropic Raman scattering (shifted to the origin and normalized) f through the Fourier transformation:

$$C(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(v) e^{-ivt} dv$$

```
// name: AM-pure Raman, anis
// spectrum is normalized

// fundamental transition:
var s0_f = 16.12740;
var sigma_f = 16.37161;
var rmax_f = 2252.629889;

// hot band:
var s0_h = 4.214350;
var sigma_h = 7.628148;
var rmax_h = 2253.718271;

// nju3 & nju4
var s0_n34 = 2.938491;
var sigma_n34 = 10.243216;
var rmax_n34 = 2292.763764;
```

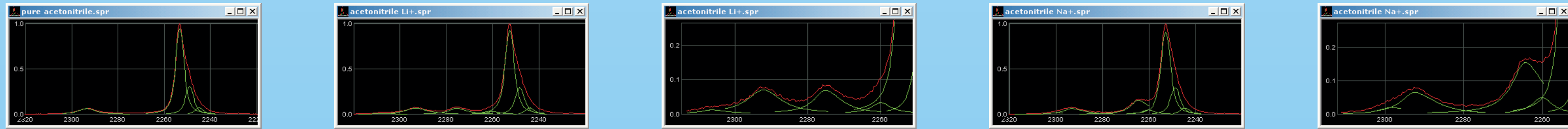
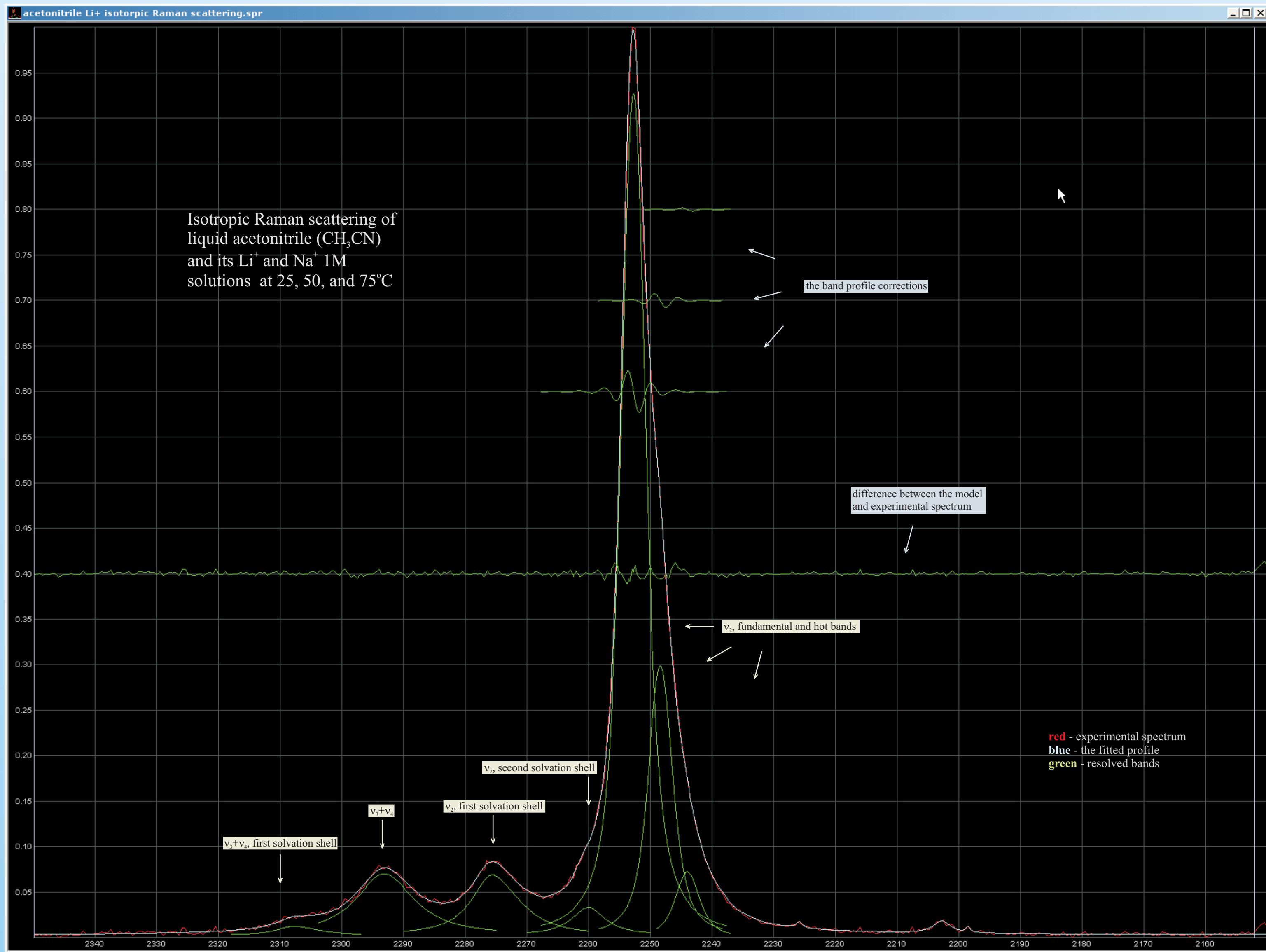
The fitting algorithm together with specific theoretical models is implemented in the software package "Spectra Handler" [T. R. Griffiths, D. A. Nerukh, and A. Eremenko, Phys. Chem. Chem. Phys., 1, 3199 (1999)]. It incorporates an "Interpreter" of math-like language for describing band profiles. Besides standard profiles like Lorentzian or Gaussian the bands can be directly expressed as the correlation functions in time domain. Robust method of fitting provides unique results for very large number of fitting parameters: 30, 40, and even more.

The package is free and can be downloaded from <http://www.chem.pwlf.cam.ac.uk/~dn232/software/>

It has been successfully used in several research groups across Europe for fitting various types of spectra.

It has been successfully used in several research groups across Europe for fitting various types of spectra.

```
file: confidence.job
      S0_f = 5.472e+0 +- 1.803e-2 ( 0.33% )
      sigma_FL = 2.498e+0 +- 5.436e-2 ( 2.18% )
      sigma_FG = 7.717e+1 +- 3.918e-2 ( 5.08% )
      nmax_f = 2.253e+0 +- 7.380e-6 ( 0.00% )
      ta_nju_hot = 4.182e+0 +- 2.905e-2 ( 0.69% )
      dwin_S0 = 8.050e+3 +- 4.534e-4 ( 5.63% )
      dwin_v = 1.613e+0 +- 3.939e-2 ( 2.44% )
```



Structure and dynamics of liquid electrolyte solutions

Structure

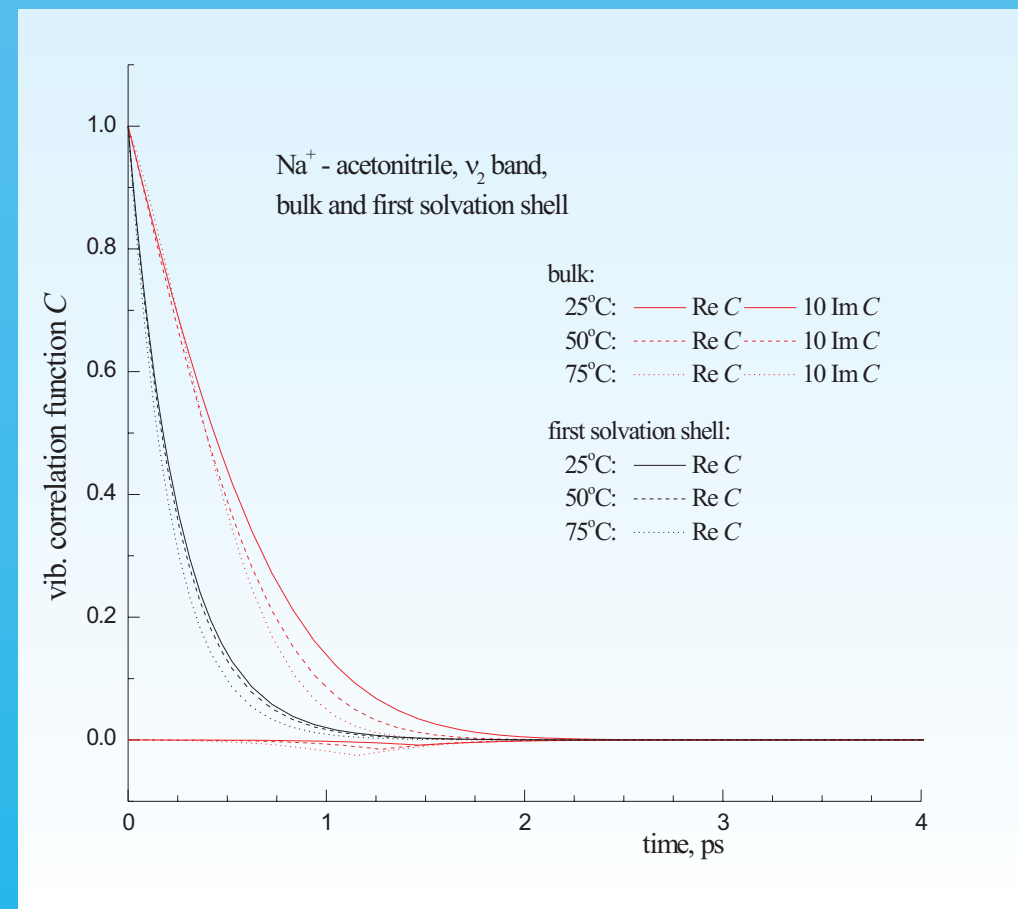
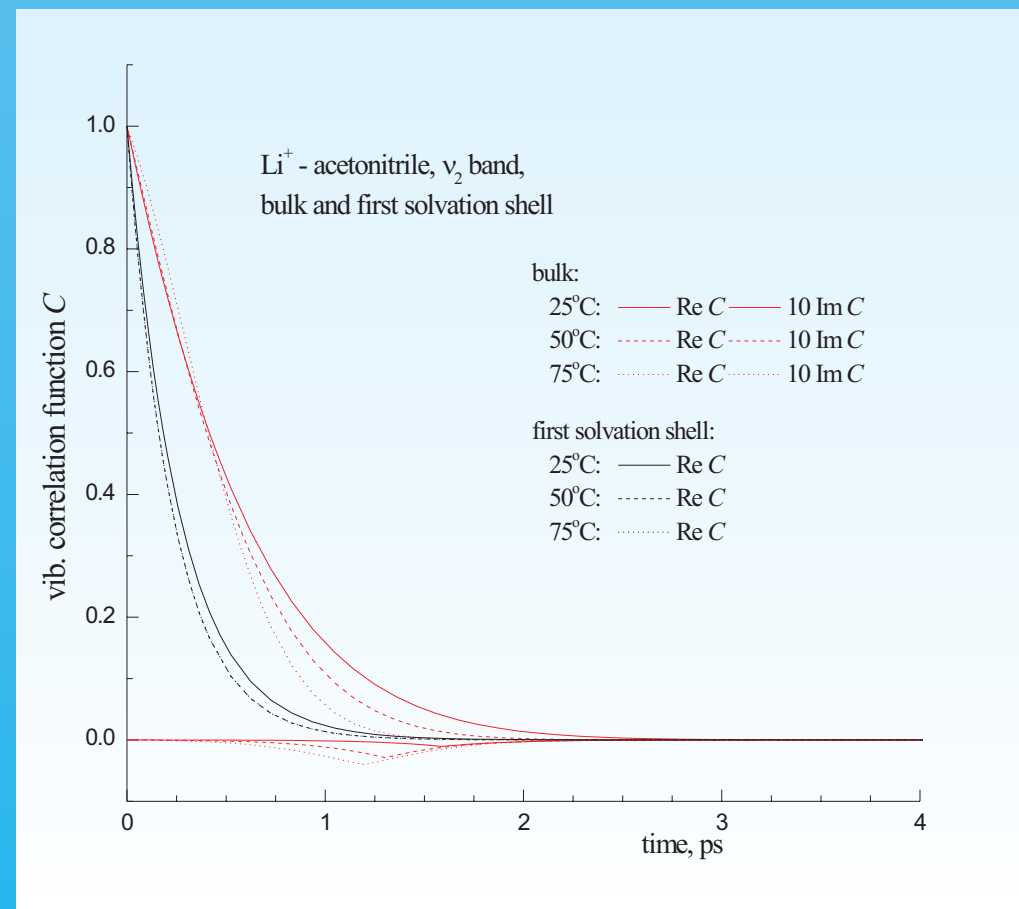
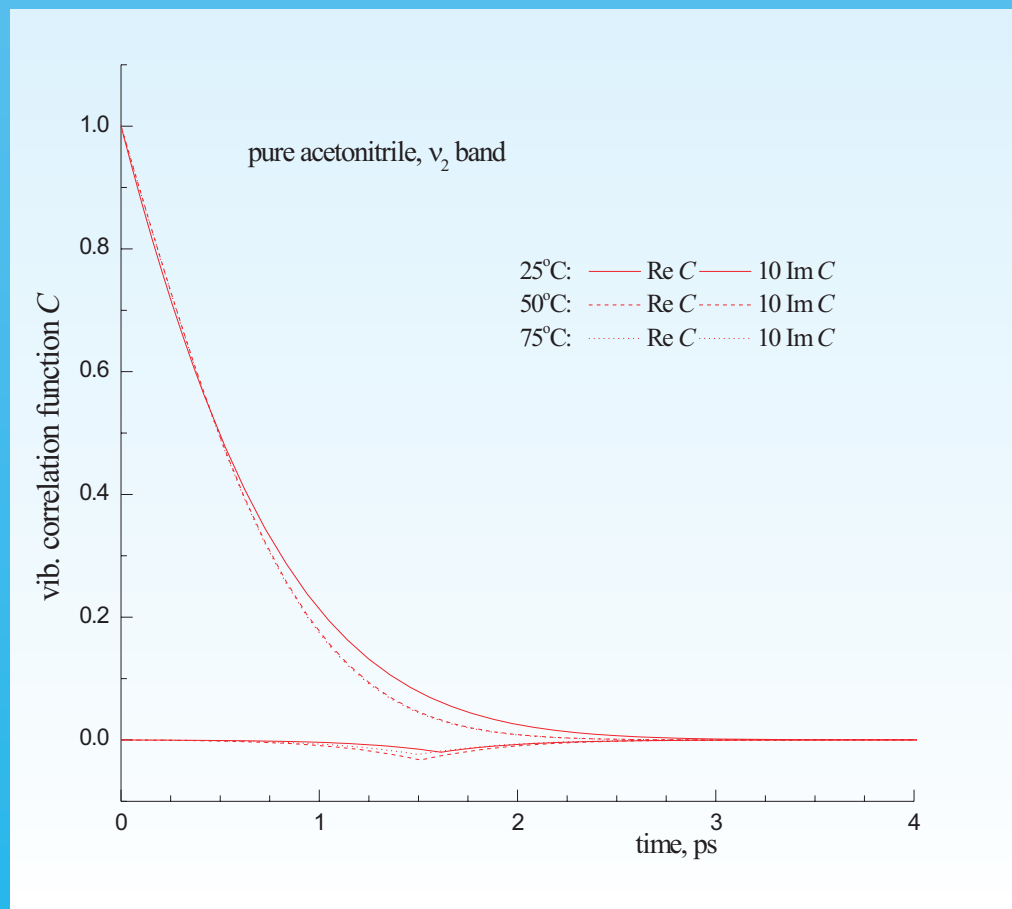
The spectra permit the distinction of three kinds of acetonitrile molecules in liquid electrolyte solution: (i) the **bulk** molecules, (ii) the molecules in the **first solvation shell**, and (iii) the molecules in the **second solvation shell**.

The appearance of the second solvation shell band indicates that the **life time** of these solvent molecules is greater than $\sim 10^{-12}$ s.

All three sorts of molecules change their intramolecular characteristics in the electric field of the ion. This is reflected in the **shifts** of their vibrational transitions. For the bulk this shift is equal to 0.53 cm⁻¹ in the Li⁺ solution and 0.39 cm⁻¹ in the Na⁺ solution.

The shifts in the solvation shells are:

- first shell: -22.8 (Li⁺), -11.7 (Na⁺);
- second shell: -6.8 (Li⁺), -7.0 (Na⁺).



Vibrational autocorrelation function

The real part of the vibrational autocorrelation function exhibits faster decay at high temperatures. The imaginary part of the vibrational autocorrelation function can not be neglected especially at higher temperatures. It also shows the temperature and ion presence dependence.

Summary

The statistically **rigorous** methodology is applied for extracting structural and dynamical characteristics of the liquid electrolyte solutions.

The **real and imaginary** parts of the vibrational autocorrelation function is obtained for the bulk acetonitrile molecules.