

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

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The method

models and data

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

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

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

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.

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.

statistically rigorous deducing the correct model

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. Ereminenko, *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:

If the solution is not unique (the outliers are substantial) the model is simplified.

The confidence intervals are calculated using the Monte Carlo method:

1. From the fitted profile using the experimental standard deviations of 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 is simplified.

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.

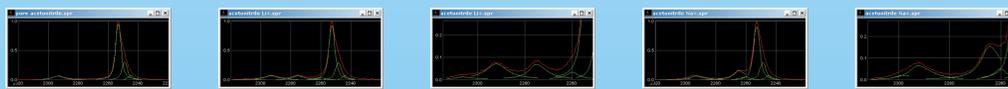
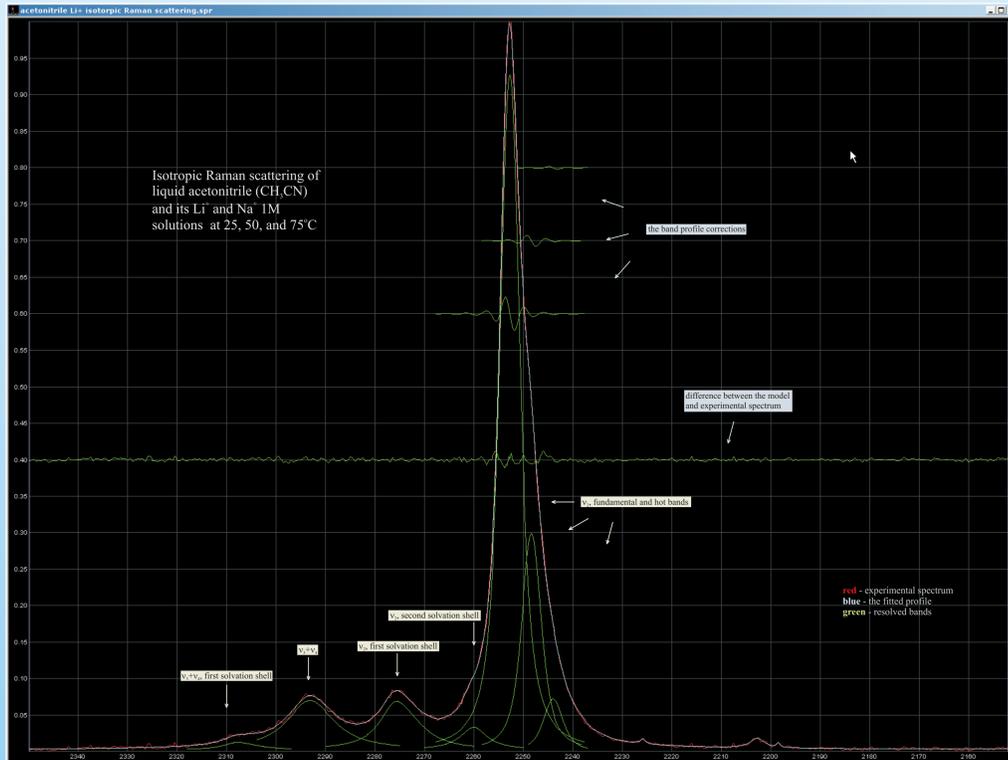
The **structural and dynamical characteristics** are obtained from the parameters of the fitted profiles.

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 structure.

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) through the Fourier transformation:

$$C(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$



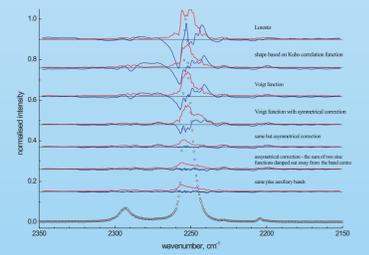
The results

The set of bands and their shape

The set of bands used to resolve the spectra was based on the gas-phase data and physical assumptions. The introduction of unidentified bands was made only if the spectral profile itself strongly suggested so.

The hierarchy of the models ranged from the simple Lorentzians to the profiles obtained by the Fourier transforms of the time-domain models for vibrational relaxation in liquids by Bratos and Tarjus [5, Bratos, G. Tarjus, *Phys. Rev.*, 24A, 1591 (1981)]. Nevertheless even the most elaborate models of the symmetric bands were not capable to reproduce the profile rigorously correct.

Thus, the use of the asymmetric corrections to the spectral bands was necessary [Dmitry Nerukh and Trevor R. Griffiths, *Phys. Chem. Chem. Phys.*, 9(10), 1799 (2001)].



The final form of the corrections introduced only two additional parameters being at the same time very close in shape to the sum of two damped sine functions:

$$y^{sym} = S/f(v) \sin(\omega v)$$

where f is a band shape and the adjusting parameters are S and ω .

The bands used for resolving the spectra were:

1. fundamental vibration ν_1 ;
 2. four hot bands of ν_1 ;
 3. combination $\nu_1 + \nu_2$ band and one hot band for it;
 4. several minor auxiliary bands.
- For the electrolyte solutions additionally were used:
5. fundamental ν_2 vibration of the first solvation shell molecules;
 6. its four hot bands;
 7. ν_2 band of the second solvation shell molecules.

For the bulk fundamental bands the Voigt band shape were used. For the fundamental bands and their hot satellites the asymmetrical corrections were used.

Structure and dynamics of liquid electrolyte solutions

Structure

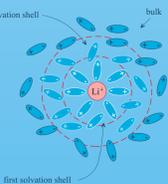
The spectra permit the distinction of three kinds of acetonitrile molecules in liquid electrolyte solution: (i) the **bulk** molecules, (ii) the molecules in the **first solvation shell**, and (iii) the molecules in the **second solvation shell**.

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

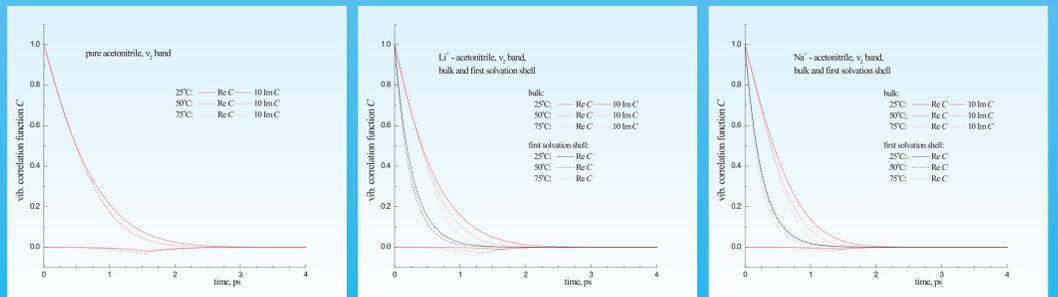
All three sorts of molecules change their intramolecular characteristics in the electric field of the ion. This is reflected in the **shifts** of their vibrational transitions. For the bulk this shift is equal to 0.53 cm⁻¹ in the Li⁺ solution and 0.39 cm⁻¹ in the Na⁺ solution.

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. The vibrational relaxation of the molecules in the first solvation shell is significantly faster. This proves the more ordered, less random character of the environment fluctuation in the vicinity of the ion.

Summary

- The statistically **rigorous** methodology is applied for extracting structural and dynamical characteristics of the liquid electrolyte solutions.
- The existence of $\sim 10^{-10}$ s. long living species in the **second** solvation shell of the ion is demonstrated.
- The **real and imaginary** parts of the vibrational autocorrelation function is obtained for the bulk acetonitrile molecules.
- The vibrational dynamics of the molecules in pure acetonitrile, in the bulk, and in the first solvation shell is analysed and compared.

The implementation

The fitting algorithm together with specific theoretical models is implemented in the software package "Spectra Handler" [T. R. Griffiths, D. A. Nerukh, and A. Ereminenko, *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.



```
// name: fit-pure-Raman-convol
// spectrum is normalized
// fundamental transition:
var fit_1 = 10.12740;
var fit_2 = 16.31451;
var fit_3 = 2252.62889;
// hot band:
var fit_4 = 4.216350;
var fit_5 = 1.826448;
var fit_6 = 2252.116771;
// asym:
var fit_7 = 2.038881;
var fit_8 = 10.243216;
var fit_9 = 2252.763764;
// Lorentzian:
var fit_10 = 1.0;
var fit_11 = 0.100000;
var fit_12 = 0.100000;
var fit_13 = 0.100000;
var fit_14 = 0.100000;
var fit_15 = 0.100000;
var fit_16 = 0.100000;
var fit_17 = 0.100000;
var fit_18 = 0.100000;
var fit_19 = 0.100000;
var fit_20 = 0.100000;
var fit_21 = 0.100000;
var fit_22 = 0.100000;
var fit_23 = 0.100000;
var fit_24 = 0.100000;
var fit_25 = 0.100000;
var fit_26 = 0.100000;
var fit_27 = 0.100000;
var fit_28 = 0.100000;
var fit_29 = 0.100000;
var fit_30 = 0.100000;
var fit_31 = 0.100000;
var fit_32 = 0.100000;
var fit_33 = 0.100000;
var fit_34 = 0.100000;
var fit_35 = 0.100000;
var fit_36 = 0.100000;
var fit_37 = 0.100000;
var fit_38 = 0.100000;
var fit_39 = 0.100000;
var fit_40 = 0.100000;
```

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

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

```
job file: confidence.job
fit_1 = 10.12740 +/- 1.805e-2 ( 0.178 )
fit_2 = 16.31451 +/- 3.318e-2 ( 0.203 )
fit_3 = 2252.62889 +/- 7.358e-2 ( 0.033 )
fit_4 = 4.216350 +/- 2.955e-2 ( 0.070 )
fit_5 = 1.826448 +/- 4.182e-2 ( 0.229 )
fit_6 = 2252.116771 +/- 4.334e-2 ( 0.192 )
fit_7 = 2.038881 +/- 1.633e-2 ( 0.080 )
fit_8 = 10.243216 +/- 1.835e-2 ( 0.180 )
```