carried out giving some theoretical background on the basis of quantum chemistry for this fundamental process of solution chemistry.

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Solute–Solute Interactions by NMR of Molecules Dissolved in Liquid Crystal Solvents: Pyridine – Iodine Molecular Complex in Nematic Phase

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NMR spectra of pyridine [^{14}N] and pyridine [^{15}N] partially oriented in nematic phase IV in presence of iodine show an increasing width as a function of the I_2 concentration. The observed spectral changes can be interpreted assuming that, as the molecular complex between iodine and pyridine is formed, a considerable variation in the orientation of pyridine moiety is produced.

Spectral analysis, performed by means of LEQUOR programme, reveals that the direct dipolar couplings (D_{ij}) are linearly dependent on the iodine concentration.

Our attempts to interpret the measured couplings on the basis of an average geometry and orientation of pyridine were unsuccessful leading to dramatic distortion effects on the apparent geometry. These results suggest that a two sites exchange mechanism is operating in the nematic phase, the two sites being the free pyridine and the complexed one.

By taking account of this exchange and using ^{15}N enriched pyridine an attempt was made to obtain the geometry and orientation of the pyridine–I_2 molecular complex.

Nuclear Quadrupole Coupling Constants of Small Ions in Aqueous Solution

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An atomic nucleus with a spin quantum number $I > ½$ possesses a nuclear quadrupole moment, which, when interacting with an external electric field gradient, gives the so-called quadrupole coupling. This coupling plays a dominating role for the relaxation rates of NMR signals of quadrupolar ions [1], but it can also give additional splittings of signals in systems, where the field gradient does not average to zero at the nuclear site.

However, for a dilute aqueous solution of ions, the field gradient is caused by the surrounding water molecules, which, due to their motion, will average it to zero. Hence, there is no splitting, but the fluctuation of the field gradient will contribute to the relaxation. From the NMR experiment it is possible to estimate the product between the field gradient fluctuation, $\langle V_{zz}^2 \rangle_{eq}$, and a correlation time τ_c, associated with the motion of the water molecules.

In this work we have focused our interest on the field gradient at the ion nuclear site, and the origin of it. Therefore, calculations with the Monte Carlo simulation technique have been performed on systems consisting of 50 water molecules surrounding an ion (Li^+, Na^+ and Cl^-). The configurations generated in the simulation have been used to calculate the field gradient fluctuation at the nuclear site of the ion. The results have been compared with experimental and other theoretical data.

The analytical expressions for the intermolecular pair-potentials used in the Monte Carlo program, have been obtained from fittings of accurately calculated quantum mechanical (near Hartree–Fock) energies and field gradients of *ca.* 80 ion–water molecule configurations.

In Table I the calculated electric field gradient at the nuclear site of a lithium ion, and its fluctua-

TABLE I.

N	$\langle V_{zz} \rangle_{eq}$ (a.u.)	$\langle V_{zz}^2 \rangle_{eq}$ (a.u.)
4	$2.2 \cdot 10^{-4}$	$0.3 \cdot 10^{-4}$
5	$2.9 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$
10	$-13.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
50	$23.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$
exp.	–	$0.14 \cdot 10^{-4}$