$$\text{RCOOH}\cdots\text{S} + \text{RCOOH}\cdots\text{S} \rightleftharpoons \text{RCOOH}\cdots\text{RCOOH}\cdots\text{S} + \text{S},$$

$$\text{RCOOH}\cdots\text{S} + \text{ROH}\cdots\text{S} \rightleftharpoons \text{RCOOH}\cdots\text{ROH}\cdots\text{S} + \text{S},$$

$$\text{ROH}\cdots\text{S} + \text{RCOOH}\cdots\text{S} \rightleftharpoons \text{ROH}\cdots\text{RCOOH}\cdots\text{S} + \text{S},$$

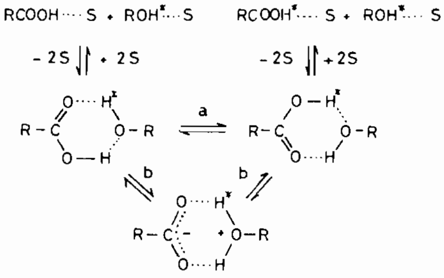
$$\text{ROH}\cdots\text{S} + \text{ROH}\cdots\text{S} \rightleftharpoons \text{ROH}\cdots\text{ROH}\cdots\text{S} + \text{S}.$$

By comparison of these data with the thermodynamic data of proton donor dimerisation in other media linear enthalpy–entropy relationships are obtained which are typical for the functional proton donor group and which are useful for estimating the degree of specific solute–solvent interactions

$$\text{AH}\cdots\text{S} + \text{S}' \rightleftharpoons \text{AH}\cdots\text{S}' + \text{S},$$

where S, S′ = THF, benzene, CCl_4, cyclohexane.

The thermodynamic and kinetic data lead to the following reaction scheme



The value of the activation entropy provides evidence against the formation of a solvated ion pair as intermediate or transition state. The mechanism of the reaction pathway a is discussed.

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Solvent Effects on Some Optical and Spectroscopic Properties of Aromatic Compounds

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In this work we want to report some solvent effects observed during studies on benzenoid and heterocyclic compounds by the Faraday effect and Depolarized Rayleigh Scattering (DRS), and their TCNE-complexes, by UV–visible spectrophotometry.

The measured properties, respectively molecular magnetooptical rotation ($[\rho]_M$), molecular optical anisotropy ($\overline{\gamma^2}$) and maximum absorption wavenumber ($\bar{\nu}_{max}$) undergo rather large changes when moving from gas phase to pure liquid or dissolved state, and vary weakly from a solvent to another one.

As regards weak interactions, the Faraday effect allows essentially to observe internal field changes (Lorentz correction). It is likely that this bulk effect is not restricted to 'aromatic' solutes. Moreover most solute–solvent interactions are masked by this non-specific medium effect, since even with polar solvents ($CHCl_3$, alcohols) no specific interaction given by π-donors and/or polar solutes (*e.g.* halobenzenes, anisole, ...) is detected. So, for a given substance, the true value of $[\rho]_M$ is obtained in the pure liquid state or in a solvent as refractive as the solute.

On the contrary, DRS, very sensitive to oriented interactions, can detect diatropism or paratropism in liquids. Therefore, to get comparable, 'intrinsic' γ^2 values one must not work with pure liquids but rather with dilute solutions in the same 'inert' solvent, that is a non-polar, weakly anisotropic one, containing bonds of the same kind as the solute. Accordingly, for organic compounds (C–H bonds), cyclohexane is preferred to CCl_4 (which may also give specific interactions). On the other hand the molar volume of the solvent need not be taken into account. The cases of benzene and some heterocyclics illustrate these principles.

Finally, spectrophotometric studies of molecular complexes show that the influence of non-polar solvents on $\bar{\nu}_{max}$ generally reduces to a gross medium effect involving a linear function of $(n^2 - 1)/(2n^2 + 1)$. As regards polar solvents, more complex interactions with aromatic compounds and acceptor are likely to occur, and no correlation can be found with polarity parameters like Z or E_T. TCNE-complexes of benzene, benzothiophene (after deconvolution of spectra) and dibenzothiophene are considered.

Two Photon Absorption and Excited Fluorescence of 2,2′-Bipyridine

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Two-photon absorption spectroscopy is proving a powerful method to probe one-photon forbidden electronic transition in molecules. Two-photon absorption occurs by a non-linear process in which two photons simultaneously interact with a molecule to induce a transition. The energy of the resultant excited state equals the sum of the energies of the incident photons. What is actually measured in such an experiment is the excited fluorescence. Three main requirements should however be fulfilled for a two-photon absorption-excited fluorescence experiment to be successfully performed. First the excitation frequency must be chosen to equal one half that of an allowed transition. Second, the sample must not absorb the excitation frequency by a one-photon process and, third, a reasonable fraction of the resultant fluorescence should occur in transparent regions of the sample. Highlights of the method are: bulk excitation is achieved for solutions prepared with optically dense solvents, one-photon forbidden electric dipole transitions of even parity, *e.g.*, g → g or u → u, can be excited; the experimental set up can be easily assembled.

This note reports on the two-photon spectra of 2,2′-bipyridine in solutions of organic non-polar solvents and in the solid state. Excitation was obtained by a nitrogen pumped dye laser with tuning ranges 5200–5900 Å, (cumarine 153), and 5650–6100 Å, (rhodamine 6G). The excited fluorescence, isolated by a filter with a 3300–4000 Å transparent window, was detected with a 1P28 photomultiplier tube. The anode current was fed to a Box-car averager for signal processing. The spectra were registered continuously by scanning the spectrum of the dye with a step motor driven holographic grating. The excited fluorescence was check to ensure a quadratic dependence on laser power. The normalized spectra of different solutions (cyclohexane, carbon tetrachloride, benzene, almost saturated) do not differ noticeably. Bands at 33613, 34246 and 34662 cm^{-1} were detected, whose assignment seems correctly be cast as ^1A_g (0–0), 0–0 + 615 (a_g) cm^{-1} and 0–0 + 995 (a_g) cm^{-1}, respectively. The 615 and 995 cm^{-1} lines are Raman active vibrational modes of trans 2,2′-bipyridine [1]. The calculated value of the ^1A_g (0–0) transition is 35945 cm^{-1} [2].

The assignment of other features, *e.g.*, 35087, 36036 and 36670 cm^{-1} seems ambiguous being, possibly, either ^1B_u (0–0) (magnetic dipole transition), ^1B_u + 1000 (b_u) cm^{-1}, ^1B_u + 1500 (b_u) cm^{-1} or ^1A_g + 1500 (a_g) cm^{-1}, ^1A_g + overtone$_1$, ^1A_g + overtone$_2$, respectively. In fact, a ^1B_u transition has been calculated at 34977 cm^{-1} [2]. All the frequencies were observed in solution and in the crystal without major differences. The decay time for fluorescence both in solution and in the crystal is of the order of few nanoseconds which would indicate a strong interaction with the environment, either solvent molecules or other molecules in the crystal.

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High and Low Affinity Ca^{++} Binding Sites in Troponin-C Studied by Synchrotron Radiation

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We have studied the structure of calcium binding-sites of Troponin-C using synchrotron radiation at the Frascati storage ring ‘Adone’. We have measured the X-ray absorption spectra of the protein. From the analysis of the X-ray Absorption Near Edge Structures (XANES) [1] we have found direct evidence of different local structures for the low and high affinity Ca^{++} sites.

Skeletal muscle Troponin-C (TNC) is one of the three subunits of Troponin which provides Ca^{++} sensitivity to myosin ATPase: this occurs only when Ca^{++}, released from sarcoplasmic reticulum, is bound to TNC. TNC belongs to a family of homologous calcium-binding proteins, which includes, among others, parvalbumins and the ubiquitous calcium-dependent regulator [2]. A common structural feature of these proteins is the presence of a number of specific Ca^{++}-binding domains referred to as EF hands [2]. EF hands were observed first in the crystal structure of carp parvalbumin and, thereafter, the presence of four EF hand structure has been predicted in TCN on the basis of the known amino-acid sequence [2]. The coordination of Ca^{++} in every EF hand so far studied can be represented by an octahedron [3]. TNC has two classes of Ca^{++}-binding sites; the first class comprises two high affinity sites for Ca^{++} (Kd = 2 × 10^{-7} *M*) which are not fully specific

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