21.2-01 THE STRUCTURES OF DITHIOPHOSPHINATE COMPLEXES OF THE LANTHANIDES IN THE SOLID AND IN SOLUTION (X-RAY + NMR). By A.A. Pinkerton, S. Spiliadis, D. Schwarzenbach, Université de Lausanne, 1005 Lausanne, Switzerland, and A-C. Söderholm, Arrhenius Laboratory, S-106 91 Stockholm, Sweden.

Extrapolation from the solid-state structure to the molecular structure in solution is a dangerous procedure; however, some knowledge obtained from X-ray diffraction may be used to interpret observations made in solution.

Crystal structures have been determined for six complexes of the type $Ln(S_2PR_2)_4^{n-}$ (Ln = lanthanide(III) or thorium (IV), R = Me, Ph or OEt). The structures are eight coordinate and dodecahedral (mmmm isomer). We have found no complex of this type with the alternative square antiprismatic structure in the solid state.

^1H and ^{31}P NMR measurements on the series $Ln(S_2PR_2)_4^-$ where R is Me, OEt or OPr^i show that there is a distinct structural break at Ho with a concomitant change in the ^{31}P hyperfine coupling. This change is shown to be from a dodecahedron to a square antiprism.

The dipolar shifts observed for the paramagnetic complexes are proportional to $(3\cos^2\theta - 1)/r^3$ where r is the distance from the paramagnetic ion to the observed nucleus, and θ is the angle between the vector r and the principal axis of the magnetic susceptibility tensor. The crystal structures above indicate that $(3\cos^2\theta - 1)$ for the ^{31}P nuclei should be about -0.6 for a dodecahedron, but close to zero for a square antiprism, whereas r should not change. This agrees with the small values of the ^{31}P dipolar shifts observed for the heavy ions compared to the light ones and with the predictions of ligand-ligand repulsion calculations.

21.2-02 PICOSECOND TECHNIQUE OF TWO-PHOTON ABSORPTION MEASUREMENT IN CRYSTALS. By B.Bareika, G.Dikčius, A.Piskarskas and V.Sirutkaitis, Faculty of Physics, Vilnius University, 232054 Vilnius,Saulėtekio al.9,Lithuania,USSR.

Picosecond light pulses of great intensity interacting in nonlinear crystals take part not only in simple processes of parametric interactions. Simultaneously such nonlinear processes as multiphoton absorption, pair generation or stimulated Raman scattering occurs.

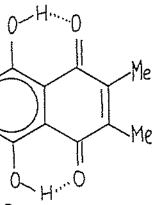
This report deals with two-photon absorption measurement in $LiNbO_3$, $LiIO_3$, Ag_3AsS_3 crystals. Our experimental setup consists of picosecond phosphate glass master laser (PL), two-step amplifier, harmonic generator on KH_2PO_4 crystal and pulse measurement technique. The energies of exciting and probe (transmitting) pulses were measured by photodetectors and processed and stored by microcomputer D3-28. We measured the energy of transmitting pulse and its dependance on pump pulse intensity. It was possible to measure transmittance of the crystal at all points of exciting pulse. For this purpose probe pulse was automatically delayed by stepmotor driven variable delay line.
First or second harmonic of PL radiation (λ = 1054 nm or λ =527 nm) as well as continuously tuned radiation was used as exciting and probe pulses. The intensity of pulses up to 40 $GW\cdot cm^{-2}$ was reached, single pulse duration being 5 ps. Two-photon absorption rate β =15 kW·cm was measured in Ag_3AsS_3,20 in $LiNbO_3$.

21.2-03 DETECTION OF PICOSECOND IR PULSES BY MEANS OF NONLINEAR CRYSTALS. By B. Bareika, G. Dikčius, A.V. Mishtchenko and V. Sirutkaitis, Faculty of Physics, Vilnius University, 232054 Vilnius, Sauletekio al. 9, Lithuania, USSR.

There are some difficulties in measuring weak ultrashort infrared light signals. Detection of such signals by means of frequency up-conversion in nonlinear crystals (with a high value of second order susceptibility) has been widely investigated recently. The mechanism of parametric mixing $w_s = w_p + w_{pr}$, where w_s, w_p and w_{pr} are the frequencies of sum, pump and probe pulses respectively is used in our experiments. It is very important that the main information of the probe pulse remains in the sum-frequency pulse. We investigated experimentally the sum-frequency generation in KH_2PO_4 and $LiIO_3$ crystals cut for oo-e interaction. Their θ is 41° and 30° respectively (θ being the angle between the pump wave vector and the z-axis). A passively mode-locked phosphate glass laser (PL) with pulse repetition rate up to 2 pps was used as a pump (G. Dikčius et al., Kvantovaja electronica (1979), 6, No. 8, 1610, Russian ref.). As a probe pulse, we used superluminescence radiation of rhodamine 6G excited by the second harmonic of PL. We found the selectivity of IR detectors on 2.5 mm long KH_2PO_4 to be Δλ = 80 Å, the probe pulse wavelength being λ = 580 nm; Δλ = 60 Å in the case of 5 mm long $LiIO_3$; and Δλ = 150 Å in the case of 1 mm long KH_2PO_4. W_{pr} was tuned from 550 nm to 1500 nm.

21.3-01 INTERNAL ROTATION BARRIER CALCULATIONS BY THE SCF INDO OPEN SHELL METHOD IN THE 2,3-DIMETHYL-NAPHTHAZARIN RADICAL ANION. By C. Sieiro, Y.G.Smeyers and R.Coy-Yll, Dpt.Electrochem.Univ.Autónoma(Madrid);Inst.Rocasolano(Madrid) and Dpt.Crystallography(Sevilla)SPAIN.

We have obtained the 2,3-dimethyl-5,8-dihydroxy-1,4-naphthosemiquinone radical anion by electrochemical reduction of 1 at constant potential of -0.6 V versus sce electrode. Analysis of the epr spectrum gives the following hyperfine coupling constants: $a_H(ring)=2.6$ G, $a_H(OH)=0.61$ G and $a_H(CH_3)=1.9$ G. The equivalence of the six methyl protons as deduced from the spectrum indicates that in the time scale of epr measurements, the two methyl groups freely rotate. In order to explain this free rotation we have previously made a study of a general potential energy function of two coupled rotors(Y.G.Smeyers,Int.J.Quantum Chem.,in press). The potential energy function in the present case(C_{2v} symmetry) is deduced to be:



1

$$V(\theta_1,\theta_2) = A_{00}^{cc} + A_{01}^{cc}[\cos3\theta_1 + \cos3\theta_2] + A_{11}^{ss}\cdot[\sin3\theta_1\sin3\theta_2] + A_{12}^{cc}[\cos3\theta_1\cos6\theta_2 + \cos6\theta_1\cdot\cos3\theta_2] + A_{02}^{cc}[\cos6\theta_1 + \cos6\theta_2] + A_{22}^{cc}[\cos6\theta_1\cdot\cos6\theta_2]$$

where the possible non-equivalent conformations between the two methyl groups are: