

**Investigation of Polarized Infrared Spectra
of the Hydrogen Bond in Molecular Crystals.
New Spectral Effects in the Vibrational Spectroscopy
of Hydrogen Bonded Systems**

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A review of the experimental as well as of the theoretical studies, performed on the area of the infrared spectroscopy of hydrogen bonded molecular crystals, is given. Discussion of some physical phenomena is presented, responsible for basic spectral effects registered in the infrared spectra, as breaking of vibrational dipole selection rules in the IR spectra, linear dichroic as well as temperature effects, observed in the frequency range of the proton stretching vibrations. Also some newly recognized H/D isotopic effects for hydrogen bonded systems are presented, deduced from a quantitative analysis of the polarized spectra in the IR, namely the so called isotopic “*self-organization*” effects and the “*long-range*” H/D isotopic effects.

The Syntheses, Crystal, Molecular and Electronic Structures of $[\text{ReBr}_3(\text{py})_3]_{0.42}[\text{ReBr}_2(\text{NO})(\text{py})_3]_{0.58}$, *trans*- $[\text{ReBr}_4(\text{OPPh}_3)_2]$ and Orthorhombic Polymorph of *mer-cis*- $[\text{ReBr}_3(\text{NO})(\text{OPPh}_3)_2]$

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$[\text{ReBr}_3(\text{py})_3]_{0.42}[\text{ReBr}_2(\text{NO})(\text{py})_3]_{0.58}$ (**1**), *trans*- $[\text{ReBr}_4(\text{OPPh}_3)_2]$ (**2**), $[\text{ReBr}(\text{NO})(\text{dppe})_2]\text{Br}$ (**3**) and orthorhombic polymorph of *mer-cis*- $[\text{Re}(\text{NO})\text{Br}_3(\text{OPPh}_3)_2]$ (**4**) complexes have been synthesized by reactions of monoclinic polymorph of *mer-cis*- $[\text{Re}(\text{NO})\text{Br}_3(\text{OPPh}_3)_2]$ with pyridine, bis(diphenylphosphino)ethane, 2,2'-bipyridine, 1,10-phenanthroline. The NO group in **1** and **4** is coordinated in a linear way. Due to nitrosyl/bromine compositional disorder, the shortening of Re–NO distance [1.68(5) Å] and the elongation of N–O bond length [1.38(10) Å] are observed in **1**. The N–O bond length in **4** is extremely short [0.94(1) Å], which results probably from steric interactions of two mutually *cis* OPPh₃ molecules and a large discrepancy of Re–O–P angle values.

UV Photoelectron Spectroscopy Studies of the Diazaxylylenes Generated from Amino(hydroxymethyl)pyridines

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Diazaxylylenes generated by 1,4-elimination of water from amino(hydroxymethyl)pyridines under flash vacuum thermolysis (FVT) conditions can be directly studied by the UV-photoelectron spectroscopy (UV-PES). The elimination of water from these compounds starts at 450°C and is completed at 500–550°C. The interpretation of UV-photoelectron spectra was supported by Density Functional Theory studies.

Polymerization of Vinyl Monomers on the High Disperse Aluminum-Containing Silica

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The interaction of vinyl monomers (styrene, butyl vinyl ether, N-vinylpyrrolidinone, vinyltrimethylsilane, methyl acrylate, vinyl acetate, and vinylacetonitrile) vapours with alumino-aerosil surface has been studied by IR spectroscopy, thermal gravimetry, field ionization mass-spectrometry, and by quantum chemical simulations. The Brønsted acidic sites of the oxide ($H_0 \leq -3.0$) were found to be capable to initiate an oligomerization of butyl-vinyl ether, styrene and N-vinylpyrrolidinone, whereas the monomers containing electron acceptor substituents (methyl acrylate, vinyl acetate, and vinylacetonitrile) are sorbed only in a physical way. The method of vapour phase oligomerization at temperatures 30–120°C has been shown to be a suitable way to produce disperse composite materials with a great content of organic matter (40–60 wt. %). Experimental and calculated absorption spectra support the idea on the formation of both monomeric and oligomeric protonated species due to adsorption of vinyl monomers on the surface of aluminum-containing silica unlike on that of pure silica.

**Study on Organic Nitrates. Part VII.
New Nitrate Derivatives of
6-Oxo-1,2,3,4-tetrahydro-6H-pyrimido[2,1-*b*]quinazoline.
Potential NO Donors**

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A series of potential NO donors derivatives of 6-oxo-1,2,3,4-tetrahydro-6H-pyrimido[2,1-*b*]quinazoline with the structure of organic nitrates was obtained. They were tested *in vitro* potentiometrically in the reaction with sulfhydryl compound L-cysteine hydrochloride monohydrate.

Synthesis and Crystal Structure of Hydrogenated Pyrazino[2,1-*a*]isoquinoline Derivatives

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Racemic amino acids (Ala and Val) were used in order to optimize the procedures and to check the stereochemical outcome of the synthesis of tetrahydroisoquinoline derivatives. The key step introduced the Pictet-Spengler condensation on ketoamides **4a** and **4b** under very mild conditions that gave predominantly (3*S**,11*b**R**)-diastereomers **6a** and **6b**. These results were confirmed by X-ray crystallography.

Experimental and Theoretical Studies on Pyrolysis of *O*-Acetyl Derivatives of β -Phenylcinnamaldehyde and Benzaldehyde Oximes

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Thermal behavior of β -phenylcinnamaldehyde and benzaldehyde oxime *O*-acetyl derivatives was studied experimentally and theoretically by the semi-empirical PM3 method. Intramolecular pericyclic mechanisms were proposed for the reactions of the *E*-isomers, intramolecular catalytic polar mechanism for elimination of acetic acid from the *Z*-isomers.

The Effect of Different Synthesis Procedures on the Texture Properties of MCM-41 Molecular Sieves Modified with Cesium

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The effect of MCM-41 modification by impregnation with cesium salt on the mesoporous structure has been studied by XRD, N₂ adsorption/desorption, electron microscopy (TEM, SEM) and FT infrared spectroscopy in the skeletal region. The MCM-41 sample prepared at room temperature is more fragile to the modification and hydrothermal treatment than the siliceous material obtained by hydrothermal method.