

Does one need a high resolution in matrix isolation studies? The symmetry changes of the $^{28}\text{SiH}_4$ molecule in low-temperature matrixes

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Today more and more researchers understand that low temperature inert matrices are not so inert. Beside the influence of matrix as media, the shift, for an example, of the frequencies of the bands in compare with the gas phase, there are many examples of so-call matrix effects. They say about sites or matrix splitting to describe some spectra features. It is connecting often with different deformation of molecules in matrices. The high symmetry molecules can be very good indicators of such deformations, since the changing of symmetry results qualitative changes in the spectra. If the band splittings are well-defined, the accurate characterization of the interaction between the molecule and the matrix environment can be performed, and the value of these splittings can serve as a benchmark for testing of the models describing such an interaction.

We present recent results [1] on $^{28}\text{SiH}_4$ in nitrogen and argon matrices in the temperature range of 7 – 20 K obtained by high resolution vibrational spectroscopy. The IR absorption spectra were recorded with a Bruker IFS 125HR Fourier spectrometer with a resolution of 0.1 – 0.01 cm^{-1} in the regions of fundamental and combinational bands. The frequencies and especially the values of splittings of the bands were determined. Additionally we paid attention to the relative intensities of split components. The study confirms the previous conclusions [2,3] that the symmetry of SiH_4 molecules changes from T_d to C_{3v} upon transition from the gas phase to the nitrogen matrix. The analysis of the spectra obtained in the argon matrix shows that under such conditions, there are at least two types of SiH_4 with symmetry of D_{2d} and C_1 . The interaction of argon matrix with a SiH_4 molecule is weak and the splitting of the band in region of ν_3 stretching band is only 0.1 cm^{-1} . However, this splitting is larger than the width of the bands and can be registered in the high resolution spectra.

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Gas to solid phase transition of theobromine: crystal vs amorphous structures

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Theobromine belongs to the xanthine alkaloid class of compounds, which include, among others, caffeine and theophylline. It is a natural product present in high amounts in cocoa. Some studies suggest that theobromine inhibits the nucleation process and crystal growth of uric acid in the human body, [1] but specific information regarding the first stages of its nucleation are still unknown. In this work, we deal with the first stages of the aggregation of theobromine to form molecular clusters, and with the interactions that govern this process.[2]

Using laser vaporization and subsequent fast cooling by supersonic expansion, we generated solid clusters containing up to four theobromine molecules. Comparison of the IR spectrum of these aggregates with the predictions obtained using computational chemistry, we were able to characterize their structure and to unravel the amorphous nucleation pathways that the aggregation process follows. Such results were correlated with the two-, three- and four-body interactions found in theobromine crystals, obtained by a slow cooling deposition process.[3] The direct comparison of this gas-to-solid phase transition obtained using different conditions (see Figure 1), allows us to build a global picture of the nucleation of theobromine.

This deep analysis of theobromine led us to conclude that formation of the crystal by slow cooling and production of the amorphous solid in the supersonic expansion exhibit similar steps, up to a point at which, they take two different pathways.



Figure 1. The structure of Theobromine and the scheme of the analysis.

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Seeing more does not necessarily mean seeing clearly

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Organic dye aggregation in aqueous solution has been addressed in many experimental studies. Generally, an aromatic stacking interaction is thought to be the cause of the aggregation. One starts with the monomer–dimer equilibrium and expects larger aggregates upon increasing dye concentration in solution. This scenario is logical when one deals with neutral species. In contrast, for charged species the Coulomb repulsion should prevent stacking. In such molecular systems, the enthalpic part of the free energy is mainly controlled by anion–cation interactions. Thus, the latter interactions cannot be excluded from the discussion.

Let us consider acridine orange (AO) as the most studied example. In basic aqueous solutions at pH > 11 the absorption of AO is centered at 430–435 nm. The absorption wavelength decreases down to 417 nm in n–heptane. In both cases one deals with a monomeric AO. We are not aware of any dependence of the absorption on the concentration of the monomeric AO in solution. In neutral and acidic aqueous solutions at pH < 10 AO becomes protonated. The corresponding absorption spectra exhibit up to three bands centered at 490, 467, and around 450 nm. The relative intensities of these bands depend on dye concentration. It has been suggested that these bands belong to a monomeric cation (AOH)⁺, a doubly–charged dimer, and more complex aggregates, respectively. The bands at 490 and 467 nm have been observed in non–aqueous solutions of (AOH)⁺ as well. The fact that such aggregates are highly charged is ignored. Of course, one can somewhat reduce the enthalpic part of the free energy by assuming that the aggregation is anion–assisted, as it happens in crystals. However, it will be done at the expense of the entropic part.

On the other hand, the structure of acid–base complexes involving heterocyclic bases have been studied in details by NMR spectroscopy. One knows how the structural patterns depend on the acidity and the structure of the proton donor, solvent properties, and temperature. This knowledge can help us to elucidate the structure of the AO–aggregates at high concentrations and improve our understanding of intermolecular interactions in solution.

Titania- and montmorillonite- photocatalyzed synthesis of methane from carbon dioxide and the subsequent formation of nucleobases on early Mars and Earth

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Photocatalytic reduction of carbon dioxide on montmorillonite and TiO₂ can explain the formation of reduced gases in neutral atmospheres. CH₄ and CO were produced during 365 nm UV irradiation of CO₂ in the presence of HCl[1]. This photocatalytic reaction represents a simulation of the Martian atmosphere. Rate constants, external quantum efficiencies and effectiveness of the reduction process are discussed and compared to those estimated on Mars. Further, subsequent reprocessing of the CO + CH₄ and N₂ containing atmosphere (with the corresponding photocatalyst still present) was exposed to shock waves induced by a high-power laser. This simulated a high energy density event (e.g. an asteroid impact) on the surface of an early planet exposed to heavy bombardment by interplanetary matter. In the resulting mixtures, glycine and RNA canonical nucleobases were found[2]. Therefore, this process provides an explanation for the creation of reduced gases, the subsequent formation of simple biomolecules from neutral CO₂ rich atmospheres and also for the origin of CH₄ on Mars. The aim of this work was not to ultimately proclaim that the Earth's early atmosphere was globally reducing. Instead, evidence is presented to support the fact that the conversion of a CO₂ atmosphere to an atmosphere containing CH₄ and CO is possible. This conversion must be considered in models of initial early atmosphere transformations[3]. Therefore, a complete pathway leading from a neutral atmosphere to the formation of nucleobases under early Earth conditions has been demonstrated. Additionally, for the first time, this pathway is discussed in relation to the conditions of Mars upon solar irradiation and upon exposure to shock waves generated by the impacts of asteroids or comets. This work is a part of a research series funded by the Czech Science Foundation (grant no. 17-05076S, 13-07724S) and by Czech Ministry of Education, Youth and Sports for EU grant No. CZ.02.1.01/0.0/0.0/16_019/0000778. Part of this work was also financed by project GAUK 16742.

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