The distinctive features of the infrared vibrational spectra of 2'-deoxyadenosine and adenosine molecules isolated in Ar matrices

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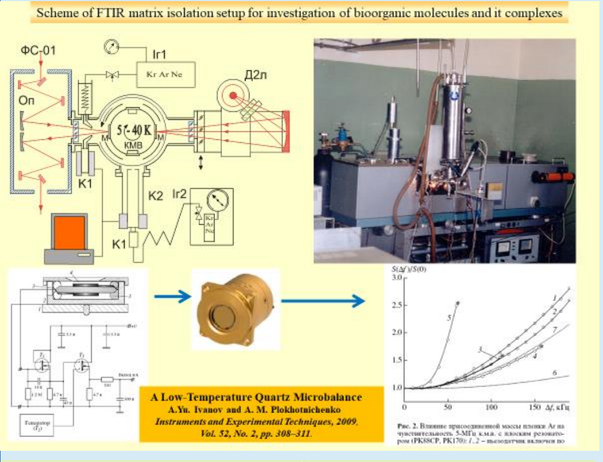
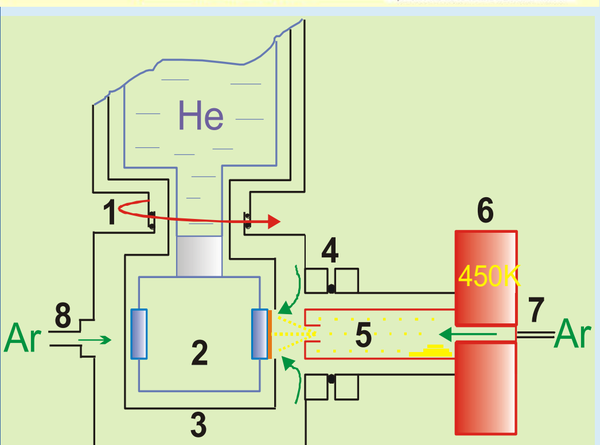
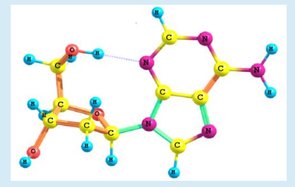
The study of the physicochemical properties of the building blocks of life in an isolation state is of fundamental interest to modern science. This interest is due to several reasons, among which are usually distinguished: a) the ability to study the internal properties of biomolecules, unperturbed by the influence of surrounding molecules, b) the possibility of a detailed, step-by-step study of intermolecular interactions, c) the ability to use high-level quantum mechanical *ab initio* calculations for the interpretation of experimental data. At different stages of such studies, biomolecules may be subjected to heating, cooling, UV irradiation, intense laser irradiation, or ionization. The behavior of biological molecules under extreme conditions can be a source of useful information for fundamental astrophysical and astrochemical studies, as well as for the practical aspects of human expansion in space.

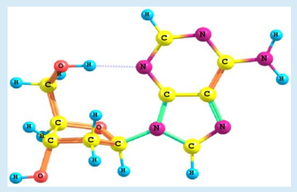
The characteristic conformational bands in the range of νOH, NH, CH stretching vibrations and UV-induced conformational transitionsons

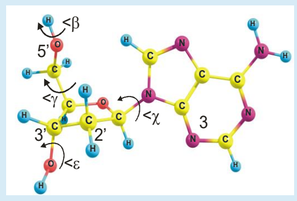




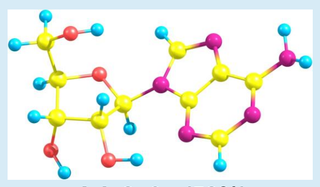
The general scheme of low-temperature setup based on liquid He cryostat: rotating vacuum seal (1), cryogenic block with cold mirrors and QCM (2), rotating nitrogen shield (3), flange with indium seal (4), Knudsen cell (5), electric heater of Knudsen cell (6), Ar flow through Knudsen cell (7), outside Ar flow (8)

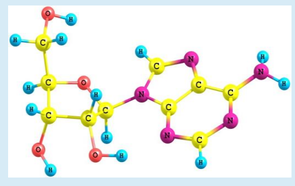


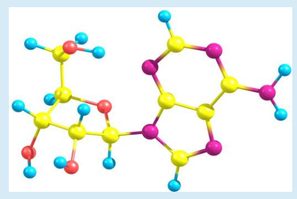


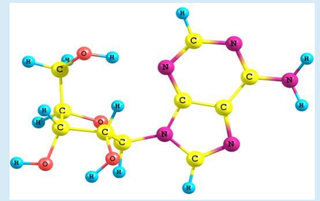


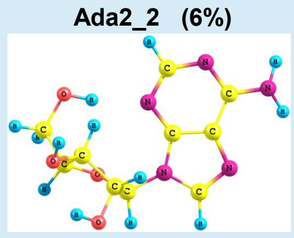
The conformers of 2'-deoxyadenosine (**dA**) that are fixed in Ar matrix and their population (%) based on ab initio calculations (**DFT/B3LYP/6-311++G(df,pd)**) and experiments











The conformers of adenosine (**Ad**) that are fixed in the Ar matrix and their population (%) based on ab initio calculations (**MP2/6-311++G(df,pd)**, **DFT/B3LYP/6-311++G(df,pd)**) and experiments

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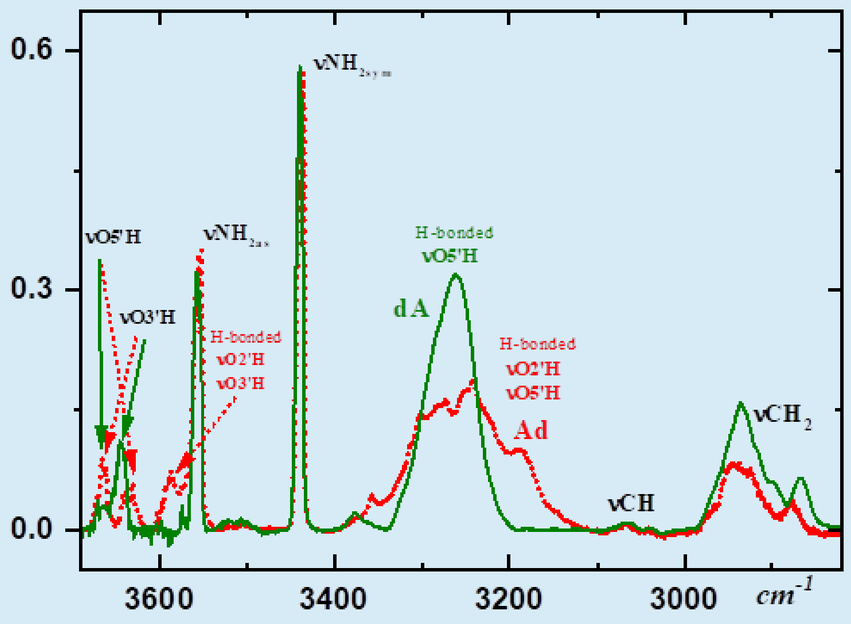
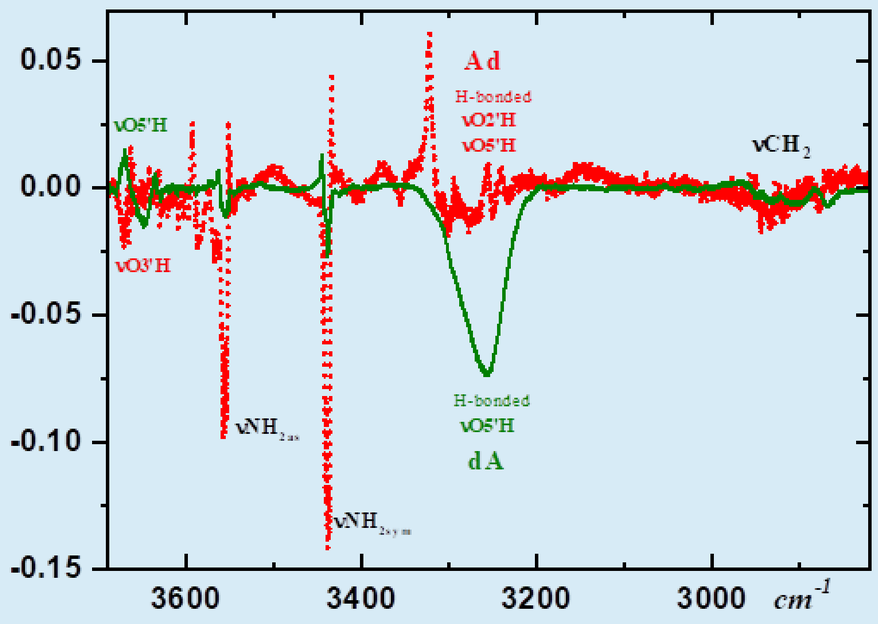
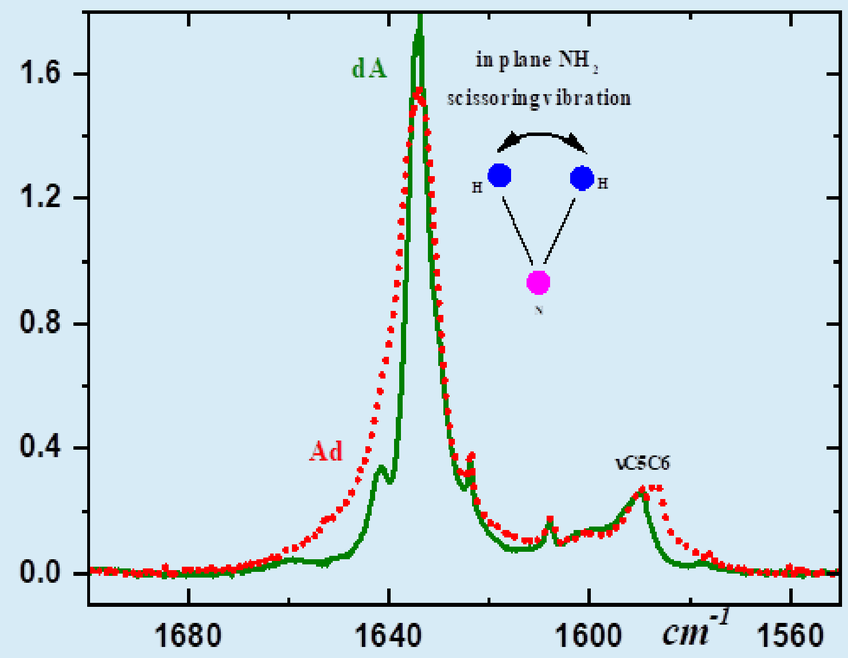


The FTIR spectra of of **dA** and **Ad** isolated in Ar matrices (T=6K) in the νOH, νNH and CH stretching region. These spectra are reduced to the same intensity of the absorption bands of NH_2 vibrations.

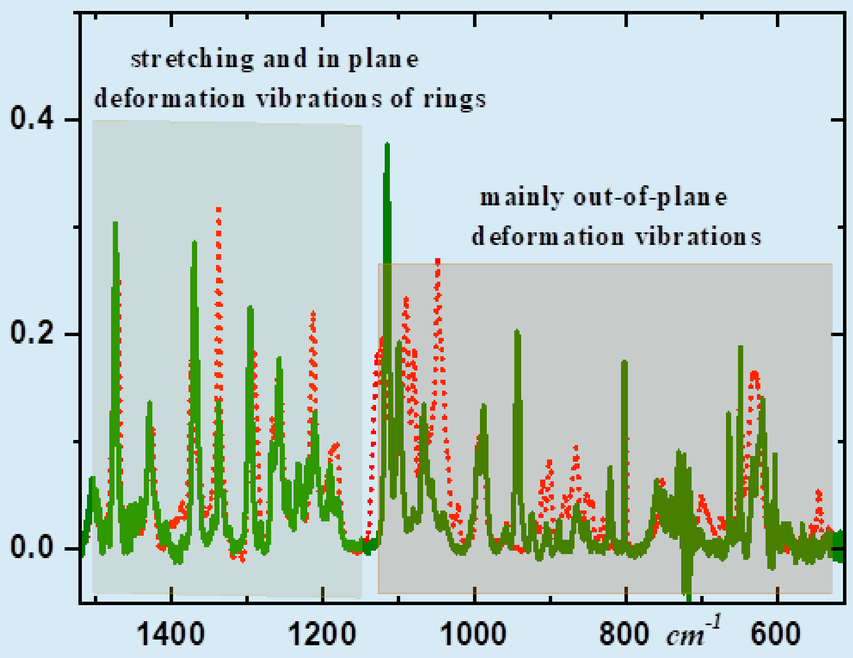


The influence of **UV-irradiation** on the FTIR spectra of **dA** and **Ad** isolated in Ar matrices in the νOH, νNH, CH stretching region. The difference spectra are shown after broadband **UV-irradiation** with deuterium lamp H4141SV (Hitachi).

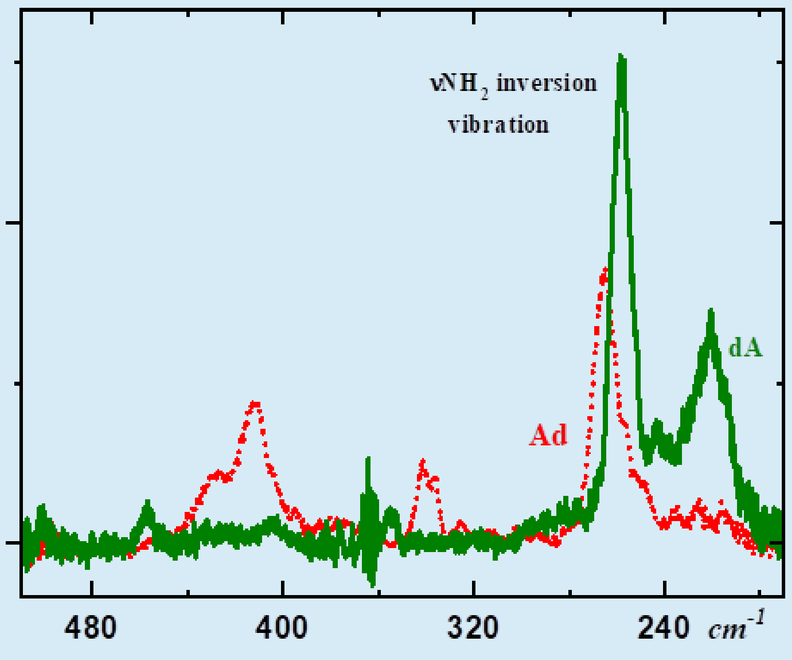
FTIR spectra of dA and Ad isolated in Ar matrices in the deformation region



The FTIR spectra of **dA** and **Ad** isolated in Ar matrices (T=6K) in region of NH_2 scissoring vibration. Unlike adeninę and isocytosine, there is no **Fermi resonance** splitting of this absorption band.



The FTIR spectra of **dA** and **Ad** isolated in Ar matrices (T=6K) in region of deformation vibrations. The best correlation between spectra of **dA** and **Ad** is observed for the region of stretching and in plane bending vibrations of the ring



The FTIR spectra of **dA** and **Ad** isolated in Ar matrices (T=6K) in the region of NH_2 inversion vibration. Unlike adenine, the absorption band of this vibration is shifted to a higher frequency region.

Conclusions

1) **Adenosine and 2'-deoxyadenosine molecules can withstand prolonged evaporation in a vacuum at a temperature of 440-470K without breaking the glycosidic bond. The conformational equilibrium between syn- and anti-subsets of these nucleosides in the gas phase is maintained when the molecules are frozen in low temperature inert matrices.**
2) **The region of νOH, νNH stretching vibrations is the most informative for experimental assessing the population of conformers.**
3) **Ultraviolet irradiation of the dA in Ar matrix increases the population of dA anti-conformers without destroying the molecule. However, UV-irradiation of Ad in Ar matrix mainly leads to the destruction of the molecule.**
4) **The best correlation between spectra of dA and Ad in deformation region is observed for the region of stretching and in plane bending vibrations of the ring**
5) **The absorption bands associated with NH_2 inversion vibration are most intense for dA.**

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