Matrix isolation FTIR and theoretical study of weakly bound complexes of isocyanic acid with nitrogen

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Non-covalent interactions are often involved in a variety of processes in biology and chemistry such as protein folding, DNA structure or molecular crystals formation. Weak molecular interactions have also an important contribution to chemical and physical processes taking place in the Earth's atmosphere.

The weak complexes of isocyanic acid (HNCO) with nitrogen were studied computationally with the use of MP2, B2PLYPD3 and B3LYPD3 methods and experimentally by FTIR matrix isolation technique. The results show that HNCO interacts specifically with N_2. Based on the AIM results it was shown that the interacting subunits are bonded either by the N-H···N hydrogen bond or by different van der Waals forces.

For the 1:1 stoichiometry, three stable minima were located on the potential energy surface. The most stable of them involves a weak, almost linear hydrogen bond from the NH group of the acid molecule to nitrogen molecule lone pair. Two other structures are bound by van der Waals interactions of the N···N and C···N types. The 1:2 and 2:1 HNCO complexes with nitrogen were optimized as well. Similar types of interactions as in the 1:1 complexes were found in the case of higher stoichiometry.

The analysis of the HNCO/N_2/Ar spectra after deposition indicates that the 1:1 hydrogen-bonded complex is prevalent in argon matrices with a small amount of the van der Waals structure also present. Annealing at 33 K leads to the formation of higher aggregates HNCO with nitrogen of the 1:2 and 2:1 stoichiometry. Both experimental and computational studies indicate that HNCO and nitrogen molecules can engage into specific intermolecular interactions leading to notable vibrational spectra changes.

In the atmospheric and space chemistry context, such interactions could become important in low temperatures, and could induce additional energy intake channels in IR and UV/VIS photon energy regions in HNCO···N_2 complexes and aggregates.