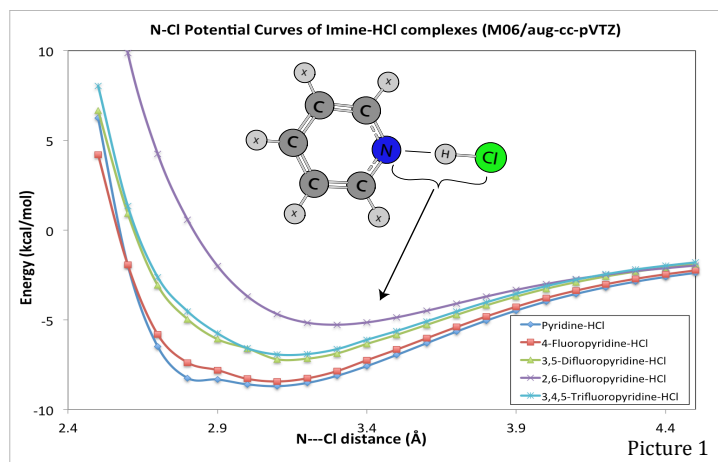


Structural and Energetic Properties of Pyridine-HCl Complexes via Computations and IR Spectroscopy

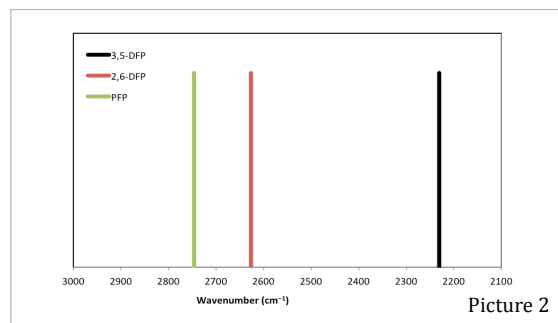
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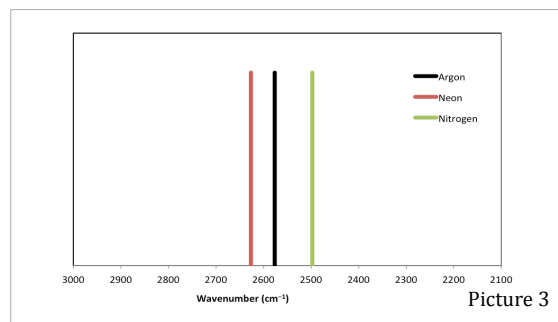
We are interested in the condensed phase effects on structure and bonding in 1:1 H-bonded complexes of hydrogen chloride (HCl) with pyridine (C_5H_5N) and its fluorine-substituted analogs; e.g., 3,5-difluoropyridine ($C_5H_3F_2N$), 2,6-difluoropyridine ($C_5H_3F_2N$), pentafluoropyridine (C_5F_5N). The interactions in these complexes range from strong H-bonds to partial H^+ transfer reactions, and we are seeking systems for which the H-bonding interaction and extent of proton-transfer are enhanced by inert, low-dielectric media (solid neon, argon, or nitrogen). We have developed an approach to model such effects by mapping N-Cl potential curves in the gas-phase and in bulk dielectric media. Presently, we also have used density functional theory (and select post-HF methods) to obtain equilibrium gas-phase structures, frequencies, binding energies, charge distributions and N-Cl potentials. We find that the addition of fluorine atoms to the pyridine ring systematically weakens the complex binding energy; fluorines adjacent to the nitrogen exert the most significant effect in terms of weakening the complex. We have also collected low temperature infrared spectra in neon, argon and nitrogen matrices, and noted that shifts in the H-Cl stretching mode reflect the strength of the H-bonding/ H^+ -transfer interactions in these complexes. To some extent, shifts in the neon matrix spectra reflect the effect of fluorines on the strength of the complexes. The matrix media also enhance the strength of the complexes and the H-Cl shifts are amplified in argon and nitrogen matrices. We are in the process of modeling these effects using continuum solvation models to represent the matrix media.



Picture 1



Picture 2



Picture 3

Picture 1 shows a comparison of all N-Cl PE curves (M06/aug-cc-pVTZ), pentafluoropyridine-HCl complex is highlighted. Picture 2 shows a comparison of different fluorinated pyridines (2,6-difluoropyridine, 3,5-difluoropyridine and pentafluoropyridine) in solid neon. Picture 3 shows a comparison of 2,6-difluoropyridine frequency shifts across different media (solid neon, argon and nitrogen).