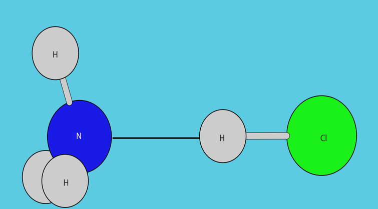
An IR and computational study of pyridine-HCl and its fluorinated analogs

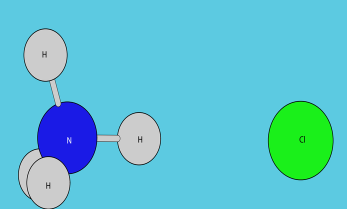
Camilla Soares & J. A. Phillips (mentor) ❖ Department of Chemistry, UWEC
Department of Chemistry, UW-Eau Claire
Eau Claire, WI 54702

University of Wisconsin Eau Claire
Chemistry

Introduction:

- **Issue:** Condensed phase effects on structure/ bonding H-bonded complexes. (e.g. H_3N-HCl, CH_3CN-HCl). A key issue is how medium effects affect extent of proton transfer:



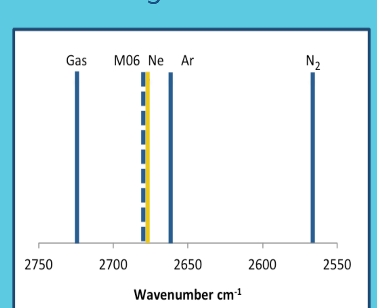


H_3N-HCl: A hydrogen bond

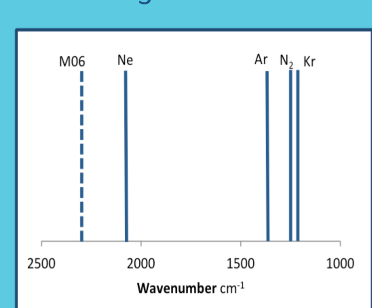
H_4N^+ Cl^-: An ion pair

- **Matrix-IR Spectroscopy:** The H-Cl stretching frequencies of H_3N–HCl and CH_3CN–HCl shift across various matrix media, indicating an enhancement of H-bond strength and H^+ transfer.[1,2]

CH_3CN–HCl



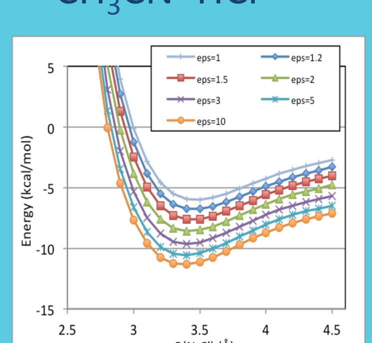
H_3N–HCl



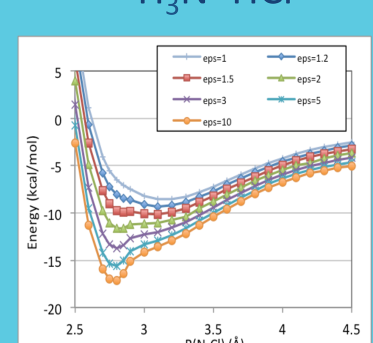
Schematics of the shift of the H-Cl stretching frequency across various media for CH_3CN–HCl (left) and H_3N–HCl (right). Note the effect is more extreme for NH_3.

- **Modeling:** We have developed an approach to model this effects by mapping N—Cl potential curves in gas-phase and dielectric media.[1]

CH_3CN–HCl



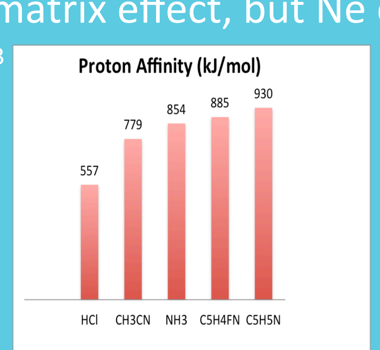
H_3N–HCl



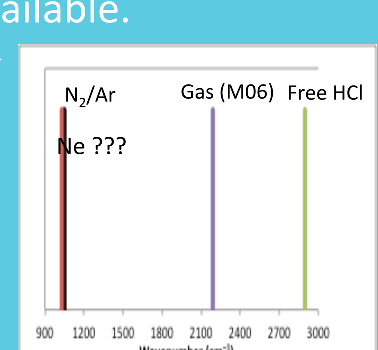
Graphs of the N-Cl potential curves in the gas phase (M06) and in bulk dielectric media (PCM) for CH_3CN–HCl (left) and H_3N–HCl (right).

- **Now:** We are exploring pyridine and its fluorinated analogs as N donors (H-bond acceptors) – varying hybridization and fluorine substitution. Our first experimental target is Pyridine-HCl because Ar/N_2 frequencies have been measured and show substantial matrix effect, but Ne data is not available.

3

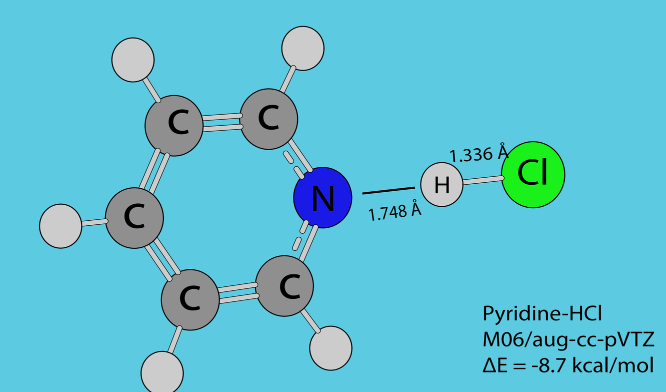


4

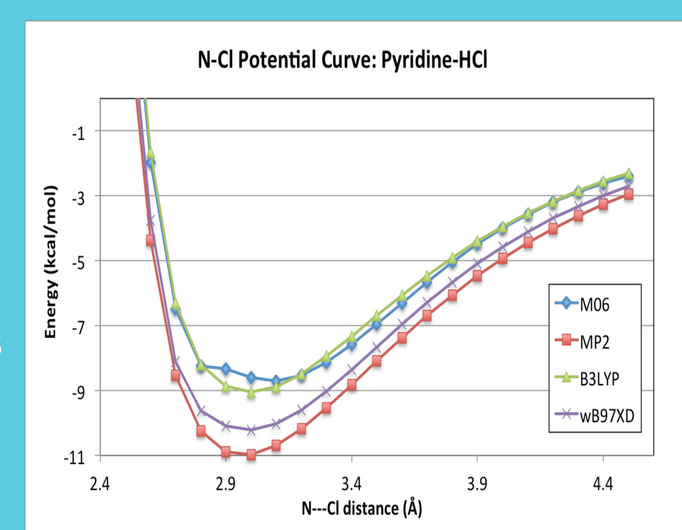


Results:

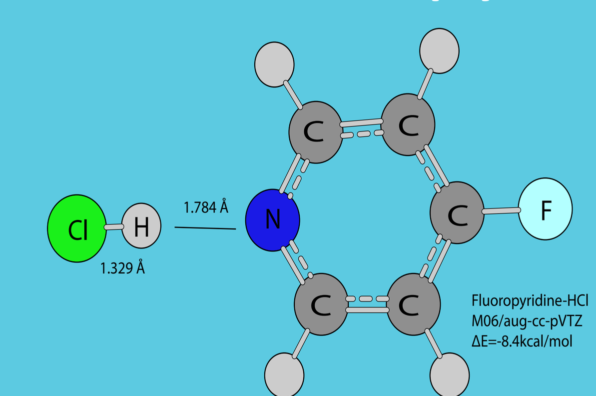
Pyridine-HCl



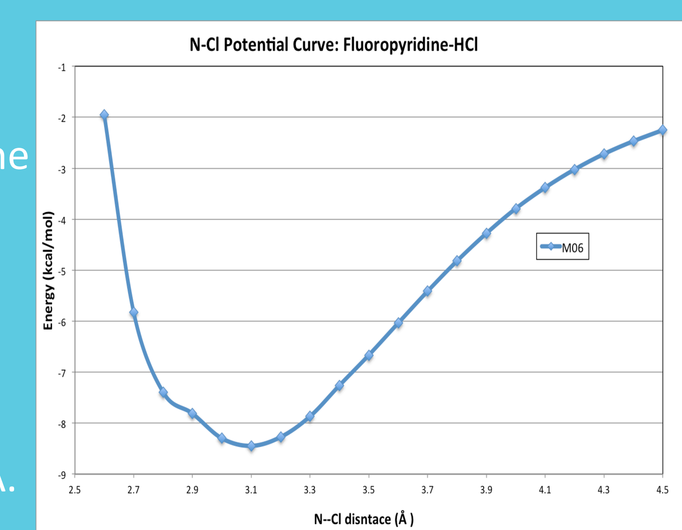
These results illustrate that pyridine is a strong H-bond acceptor and the potential curve is unusual, particularly for the M06 data.



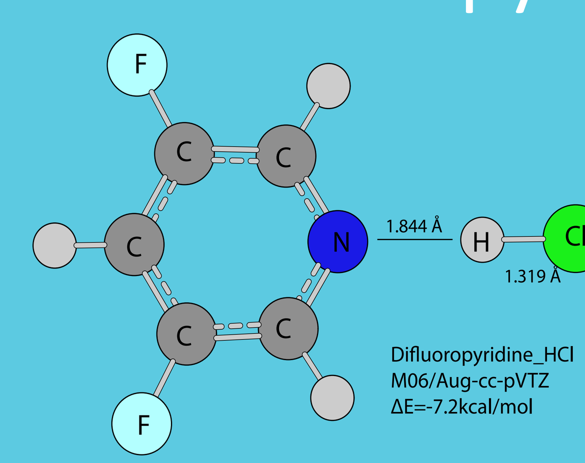
Fluoropyridine-HCl



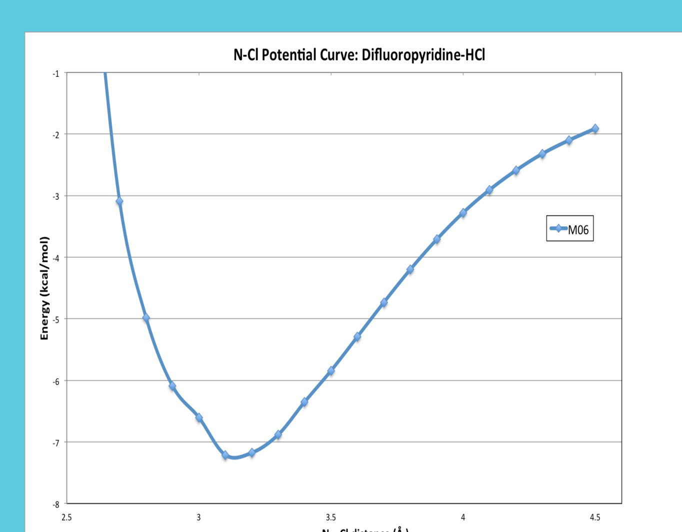
The addition of a fluorine atom to the pyridine ring weakens the complex by -0.3 kcal/mol and decreseas the H-Cl distance by 0.007Å.



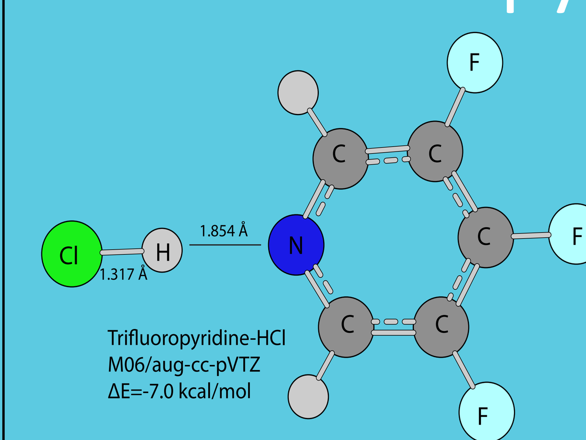
Difluoropyridine-HCl



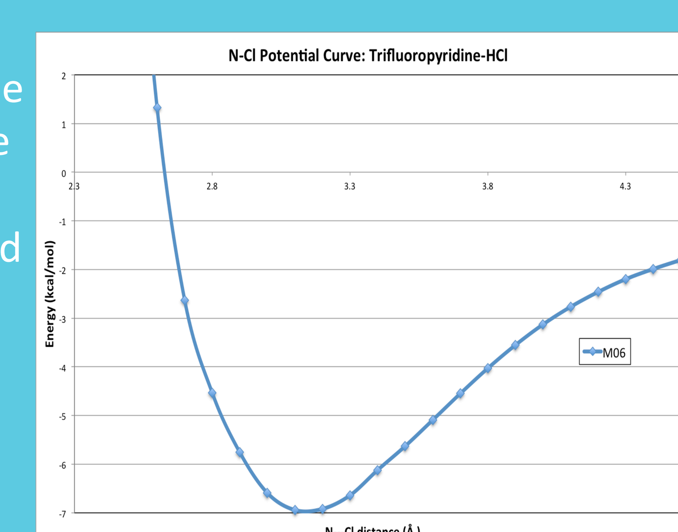
Two fluorine atoms are added to the pyridine ring; the energy shift is more significant (-0.9 kcal/mol) and the H-Cl distance is also significantly lowered by 0.017Å.



Trifluoropyridine-HCl



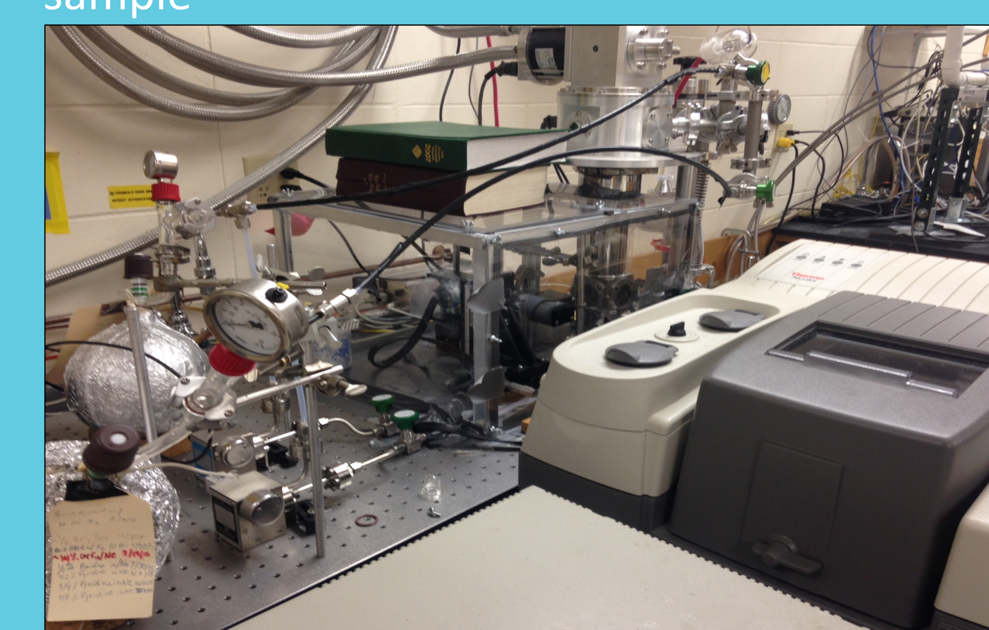
When a third fluorine atom is added to the pyridine ring, the complex is weakened but not very significantly when compared to the difluoropyridine-HCl complex.



Experiments:

Matrix Isolation Infrared Spectroscopy:

- Prepare dilute (less than ¼%) gas mixtures containing H-Cl and pyridine in neon.
- Deposit gas mixtures into vacuum chamber, where the freeze on sample mirror at 6K.
- Pyridine-HCl complexes form in the solid neon sample



Above: Matrix isolation setup, with IR spectrometer attached to sample; bulbs contain sample deposited through lines onto matrix

Above: Manifold, where gas mixtures are made under vacuum

Computational methods:

- Computer simulations of the electron distribution and bonding are used to obtain structural and energetic properties of N-HCl complexes
- Gaussian 09 version B.01 was used for all computations:
  Methods: M06, MP2, ω-B97X-D, B3LYP
  Basis set: aug-cc-pVTZ

We computed:

- Frequencies (freq)
- Binding energies
- Molecular structures (opt=tight, int=ultrafine, geom=modredundant)
- Solvation Energies

Conclusions:

- The addition of fluorine atoms also increases the H—N distance and weakens the complexes.
- The second added fluorine has the most significant effect; subsequent fluorination weakens complex only slightly.

Future Work:

- IR spectra of fluoropyridines-HCl in neon matrix
- Potentials in bulk dielectric media
- Explore different methods with the fluoropyridine complexes (M06, MP2, ω-B97X-D, B3LYP and CCSD)

Acknowledgements:

Previous work by Nikki Weiss[1]
Coworkers: Nick Hora, John Lanska, Ben Wahl
Research Support: National Science Foundation, ACS PRF, UWEC ORSP, Mercury Consortium (NSF)

Literature Citations:

1. Weiss, N. M., Waller, A. W., Phillips, J. A. *J. Mol. Struct.* **2015**, *1105*, 341.
2. Andrews, L., Wang, W., Mielke, Z. J. *Phys. Chem. A* **2001**, *105*, 6054.
3. NIST Chemistry Webbook: http://webbook.nist.gov/chemistry/pa-ser.html
4. Barnes, A. J.; Szczepaniak, K.; Orville-Thomas, W. J. Study of Intermolecular Interactions by Matrix Isolation Vibrational Spectroscopy. *J. Mol. Struct.* **1980**, *59*, 39-53.