A Computational Study of IR Frequency Shifts in $CH_3CN–HCl$

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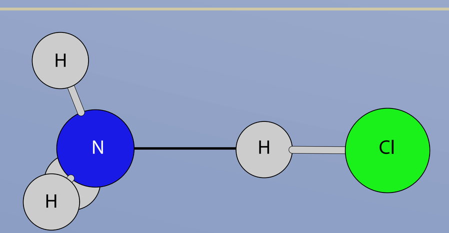
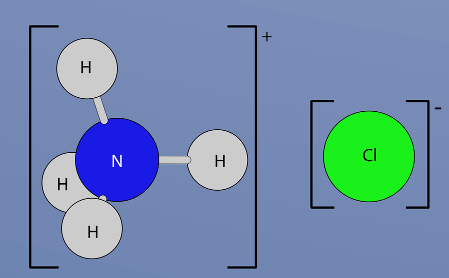
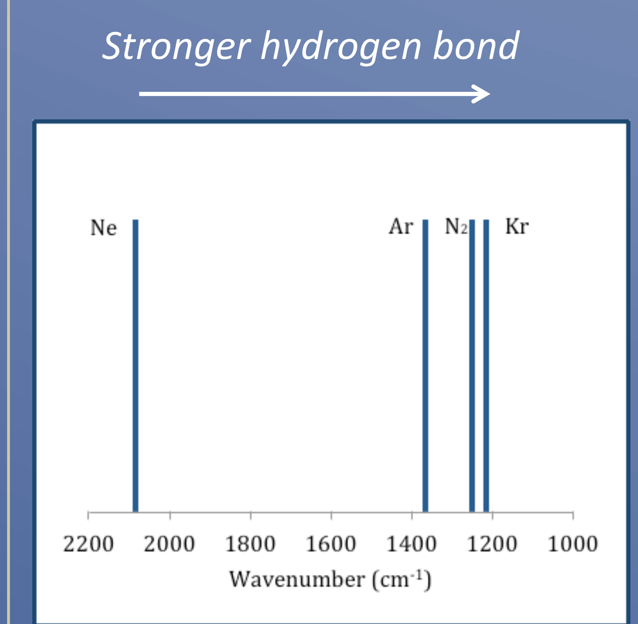
Background: $H_3N–HCl$



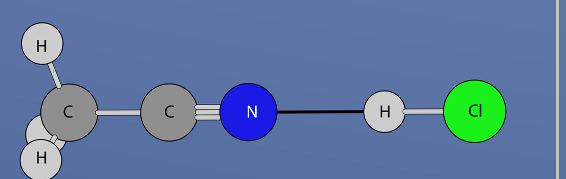
Bulk, inert condensed-phase environments cause the infrared (IR) frequency of the H-Cl bond in the complex to shift to lower frequencies. This reflects an increase in the strength of the N–H hydrogen bond with increasing charge-stabilizing ability of the environment (Ne<Ar<N_2<Kr). The extreme limit is proton transfer to make ion pairs: NH_4^+ and $Cl^–$, *e.g.*





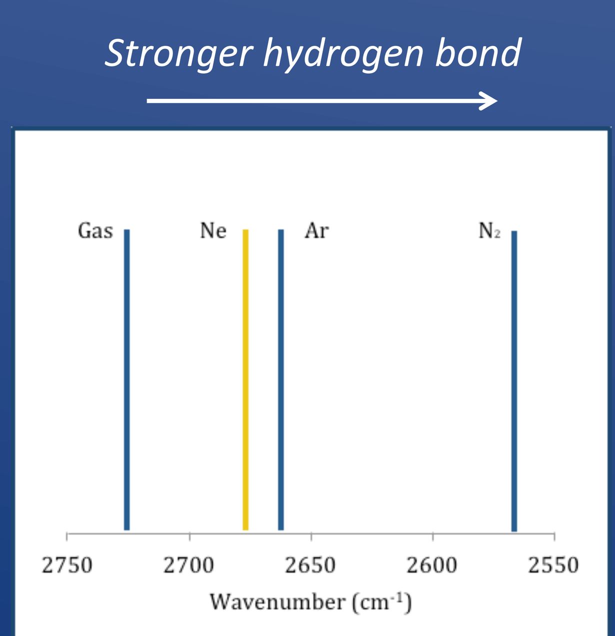
At left: Schematic of H-Cl stretching frequencies for $H_3N–HCl$ in various environments.[1] Note that a frequency shift to the right corresponds to a stronger hydrogen bond.

Present: $CH_3CN–HCl$



We observed a similar effect in $CH_3CN–HCl$ upon measuring the IR spectrum of the complex in solid neon. Because CH_3CN is a weaker base than H_3N, this effect is more subtle in $CH_3CN–HCl$ than in $H_3N–HCl$. However, the frequency shift in $CH_3CN–HCl$ is still notable, and our goal is to use computational methods to better understand the shift as well as compare and contrast it with $H_3N–HCl$.

At right: Schematic of H-Cl stretching frequencies for $CH_3CN–HCl$ in various environments.[2,3] Note that a frequency shift to the right corresponds to a stronger hydrogen bond.



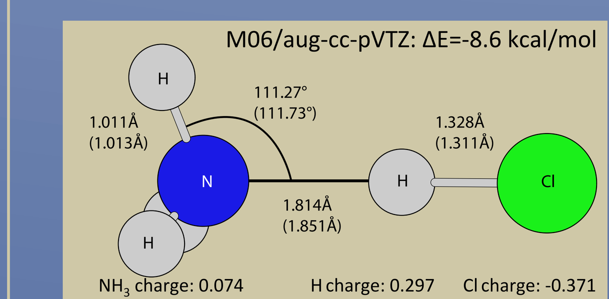
Computational Methods

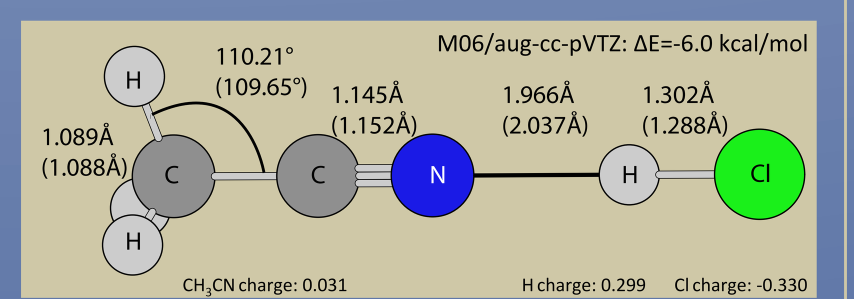
All computations were performed using Gaussian 09 versions B.01 and D.01:

- Methods: M06, MP2, and CCSD
- Basis set: aug-cc-pVTZ
- Solvation E: Polarized Continuum Model (PCM)
- Equilibrium geometries: opt=tight
- Frequencies: Scaled M06
- N-Cl potential curves: 2.3-4.5Å (0.1Å increments)
- H-Cl potential curves: 1.1-3.6Å (0.1Å increments)

Results

Equilibrium Geometries





$H_3N–HCl$ has a shorter N–H distance than $CH_3CN–HCl$; $H_3N–HCl$ also has a longer H-Cl distance (M06 and CCSD calculations reported, with CCSD results in parentheses). Furthermore, $H_3N–HCl$ also has a larger binding energy than $CH_3CN–HCl$ (-7.7 vs. -6.0 kcal/mol via CCSD) and more charge transfer.

Environmental Effects on Equilibrium Geometries

Table 1. Condensed-phase structure of H_3N-HCl vs. dielectric constant (PCM/M06/aug-cc-pVTZ)

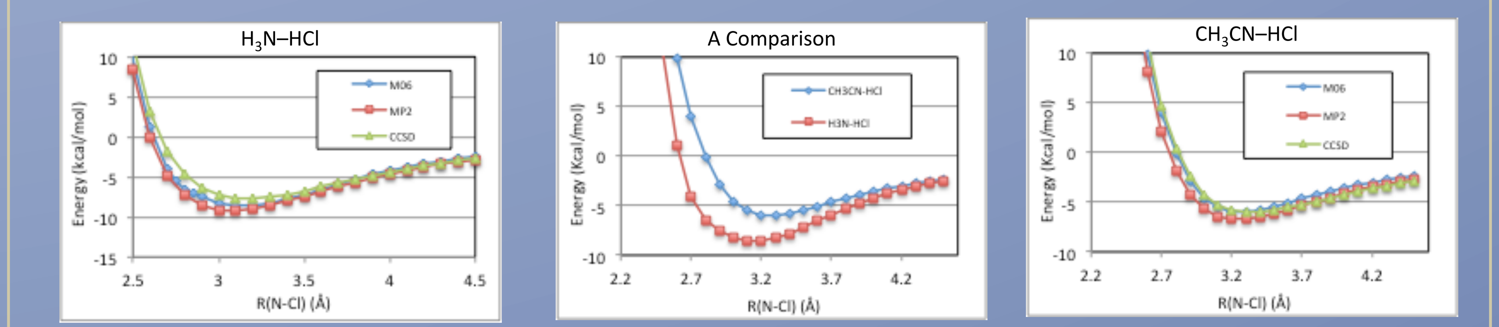
Dielelctric constant	NH distance (Å)	HCl distance (Å)
0	1.814	1.328
1.2	1.777	1.335
1.5	1.719	1.348
2	1.273	1.570
3	1.110	1.810
5	1.083	1.889
10	1.070	1.945

Table 2. Condensed-phase structure of CH_3CN-HCl vs. dielectric constant (PCM/M06/aug-cc-pVTZ)

Dielelctric constant	NH distance (Å)	HCl distance (Å)
0	1.966	1.302
1.2	1.950	1.304
1.5	1.933	1.306
2	1.912	1.308
3	1.889	1.310
5	1.869	1.313
10	1.852	1.315

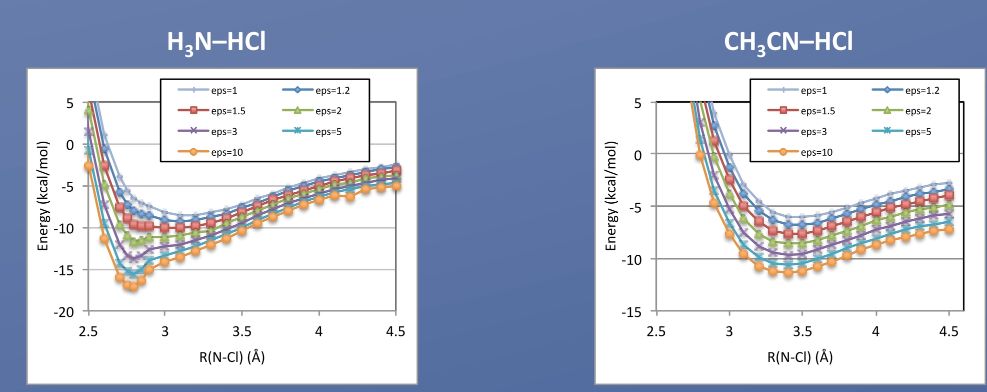
These data illustrate the contraction of the N-H distance in both $H_3N–HCl$ and $CH_3CN–HCl$ with increasing dielectric constants (PCM/M06/aug-cc-pVTZ). In $H_3N–HCl$, the N-H distance significantly contracts at ε= 2; in $CH_3CN–HCl$, the contraction of the N-H distance is more subtle.

Gas-Phase N-Cl Potential Curves



Plots of potential energy vs. fixed N-Cl distance (Å) for $H_3N–HCl$ (left) and $CH_3CN–HCl$ (right). Results are consistent across methods, though MP2 slightly overestimates hydrogen bond energy (relative to CCSD), especially for $H_3N–HCl$. Curves provide additional illustration that the H bond is stronger (*depth of curve*) and shorter (*minimum*) in $H_3N–HCl$. *Inner wall is steeper in $CH_3CN–HCl$*; ion-pair structures are higher in energy than for $H_3N–HCl$.

Condensed-Phase N-Cl Potential Curves



For $H_3N–HCl$, the shape of the curve changes dramatically with increasing dielectric constant (ε), and the minimum energy point shifts from 3.1Å (R_{NH}=1.8Å) at ε=1.2 to 2.8Å (R_{NH}=1.4Å) at ε=10. This is consistent with large shifts in the IR spectra.

For $CH_3CN–HCl$, the overall shape and minimum energy point do not change with ε value. This suggests a lack of sensitivity to the medium and is inconsistent with IR spectra,[2,3] but the shifts are subtle.

Acknowledgments

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