Condensed-Phase Effects on the Structural Properties of FCH₂CN–BF₃ and CICH₂CN–BF₃: A Matrix-Isolation and Computational Study  
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Context: Large Gas-Solid Structural Differences

- FCH₂CN–BF₃ 
  - Gas Phase 
  - Crystal Phase  
  - Δ B-N Distance = 0.787 Å 
  - Δ N-B-F Angle = 11.2° 
- CICH₂CN–BF₃ 
  - Gas Phase 
  - Crystal Phase 
  - Δ B-N Distance = 0.725 Å 
  - Δ N-B-F Angle = 11.0° 

~Extreme structural changes have been predicted between gas- and crystal-phase complexes.  
~Comparable to the largest experimentally-observed case: HCN–BF₃ (ΔR_{B-N} = 0.835 Å)²  
~The issue at this point is the effect of bulk, inert, condensed-phase media (e.g. solid argon).

Experimental: FTIR Spectra in Nitrogen, Argon, and Neon Matrices

~Frequencies shift systematically with the tendency of the medium to stabilize charge: 
   
   Gas < Ne < Ar ≤ N₂ < Crystal

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~Suggests a progressive medium-induced contraction of the B-N bond
~B-F asymmetric stretching frequencies below

Mechanism: Continuum Solvation Models

~Each curve is the sum of the gas-phase energy and the electrostatic component of ΔG_{gas} †.  

~The solvation energy is greater at shorter bond lengths, at which the complex is more polar.  
~Global minimum shifts inward -> Medium-Induced Structural Change

Conclusions

~Frequency shifts indicate of continuous structural change across a range of inert media.  
~Mechanism arises from a flat B-N potential and greater solvation energies at shorter bond lengths.

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References

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Computations: B-N Bond Potentials

~Key feature: A flat B-N bond potential  
~ΔE between 2.4 Å and 1.7 Å is only about 2-3 kcal/mol.  
~Small ΔE between bonded and non-bonded portions of the curve is critical for medium to shift minimum R_{B-N}^*  
~All computational methods are relatively consistent.