

Matrix Isolation Infrared Spectroscopic Studies of Hydrogen-Bonded Complexes



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Introduction

Molecules experience weak interactions between one another known as intermolecular forces. These forces, including London dispersion forces, Dipole-Dipole forces, and hydrogen bonding, have a great influence on the chemical properties of a substance, including density, boiling point, and crystalline structure. In particular, hydrogen bonding occurs traditionally between a hydrogen attached to an electronegative element (typically O, N, or F) and the electronegative atom of another molecule. Nonconventional hydrogen bonds have been shown to exist between a hydrogen attached to a carbon and an electronegative element.¹ In order to demonstrate this incredibly weak interaction, a technique known as matrix isolation has been used.

Matrix Isolation

In the matrix isolation technique, a guest species is isolated in an unreactive host matrix (Argon gas) at a ratio of between 1:250 and 1:1000 guest to host. In order to examine interactions between two molecules, they are isolated separately in host matrices. (see Figure 1). At low temperatures (~10 K) and pressure (10^{-7} torr), the guest-host mixtures are codeposited on a window inside a Fourier transform infrared spectrometer (FTIR). The spectrometer is used to detect changes in the infrared bending and stretching modes that can be caused by intermolecular interactions.

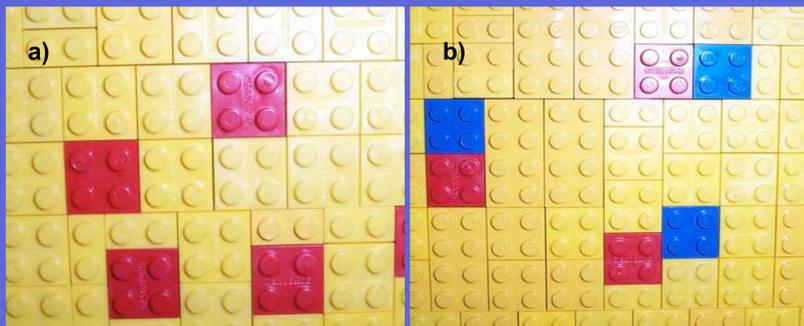


Figure 1. Representation of matrix isolation a) one chemical b) two chemicals with intermolecular forces



Figure 2. Matrix isolation apparatus.

Rector Science Complex Laboratory

In summer 2008, the matrix isolation apparatus at Dickinson College was moved to the new Rector Science complex. In this setup, a custom-made box is positioned in a spectrometer attached to a cold head. This is attached to both a turbo molecular pump (56,000 RPM) and a closed cycle helium circulator. Attached to the box are two valves for the codeposition of guest-host mixtures onto potassium bromide or calcium fluoride windows held by a copper holder insulated with indium.

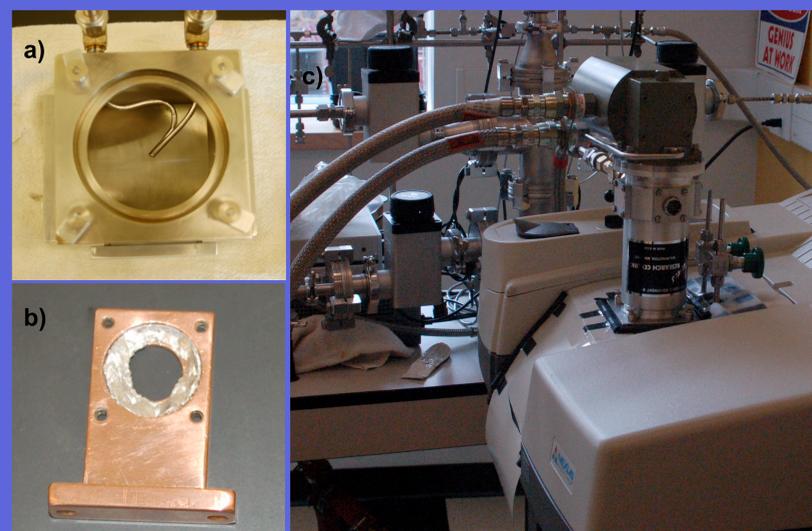


Figure 3. a) Top view of matrix isolation chamber with deposition tubes. b) Copper window holder with indium insulation. c) Cold head attached to matrix chamber in place inside spectrometer.

Previous Results – Bromocyclopropane

With the matrix isolation apparatus at Dickinson College, a hydrogen bond was shown to occur between the hydrogen attached to the substituted carbon of a bromocyclopropane ring and the nitrogen of ammonia. This represents the first example of a substituted cyclopropane participating in hydrogen bonding and the second example of an alkane taking part in a C-H...N hydrogen bond.¹

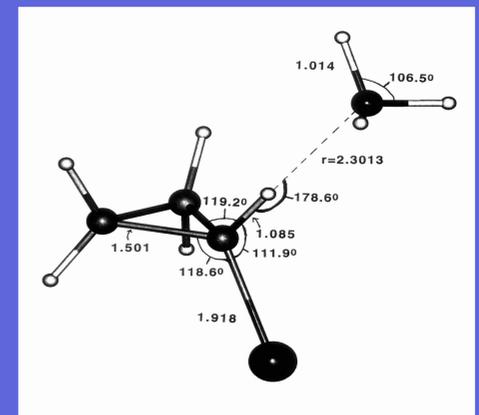


Figure 4. Schematic of hydrogen bond between bromocyclopropane and ammonia.¹

Future Work

Thin layer polymeric films can also participate in hydrogen bonding as cross-linking between multi-layered films. In particular, poly(vinylpyridine) exhibits hydrogen bonding with poly(acrylic acid) in a layer-by-layer technique.² The matrix isolation technique will be used to study the interactions between the films and deposited gases.

Acknowledgments

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References

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- (2) Hao, E.; Lian, T. *Langmuir* **2000**, *16*, 7879-7881.