Hydrogen bonds in cryogenic matrixes

WHY CRYOGENIC MATRIXES –

COLD MOLECULE SPECTROSCOPY

METHODS TO OBTAIN COLD MOLECULES

APPLICATION OF THE METHODS TO PROBLEMS OF OUR INTEREST

WHY COLD MOLECULE SPECTROSCOPY?

SPECTRA WITH SMALLER LINE WIDTHS

STUDY OF WEAK COMPLEXES

STUDY OF INTRA MOLECULAR ENERGY TRANSFER DYNAMICS

COLD MOLECULE ALONE IS NOT SUFFICIENT –

YOU NEED COLD ISOLATED MOLECULES

SPECTROSCOPISTS USE TWO POPULAR METHODS TO PRODUCE COLD ISOLATED MOLECULES

SUPERSONIC EXPANSION

MOLECULES ARE EXPANDED FROM A HIGH PRESSURE SOURCE, THROUGH A NOZZLE, CAUSING COOLING OF INTERNAL ENERGY – *SUBTLE METHOD*

MATRIX ISOLATION

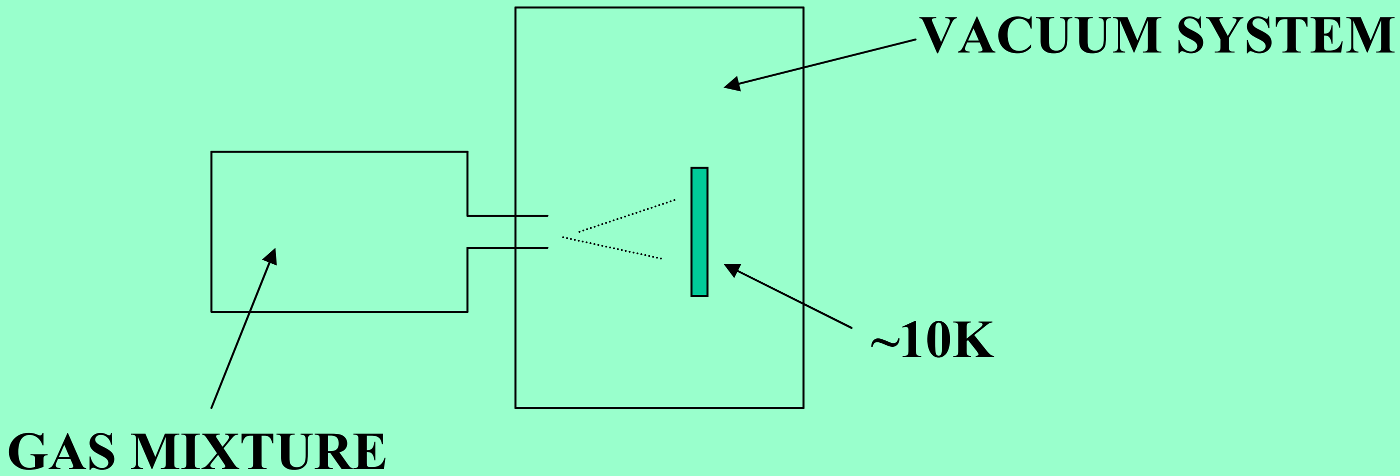
MOLECULES ARE TRAPPED IN AN INERT MATRIX ON TO A COLD FINGER - *BRUTE FORCE METHOD*

WHAT IS MATRIX ISOLATION?

MIX THE SAMPLE WITH A LARGE EXCESS OF AN INERT GAS

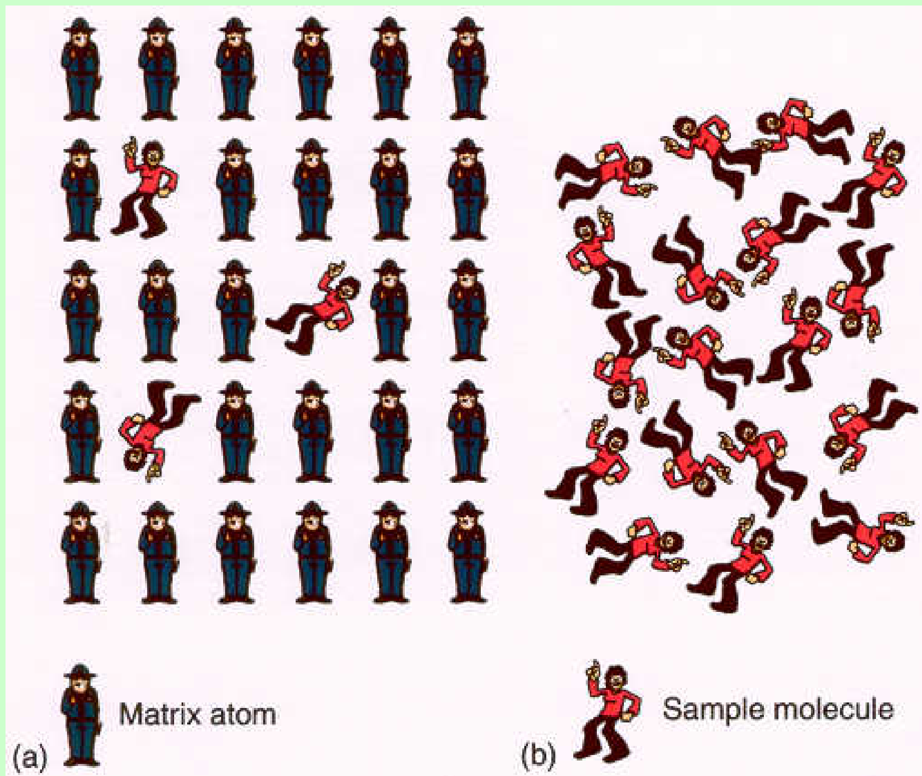
e.g. ACETYLENE IN ARGON

LARGE EXCESS ⇒1 : ~1000 OF ACETYLENE TO ARGON

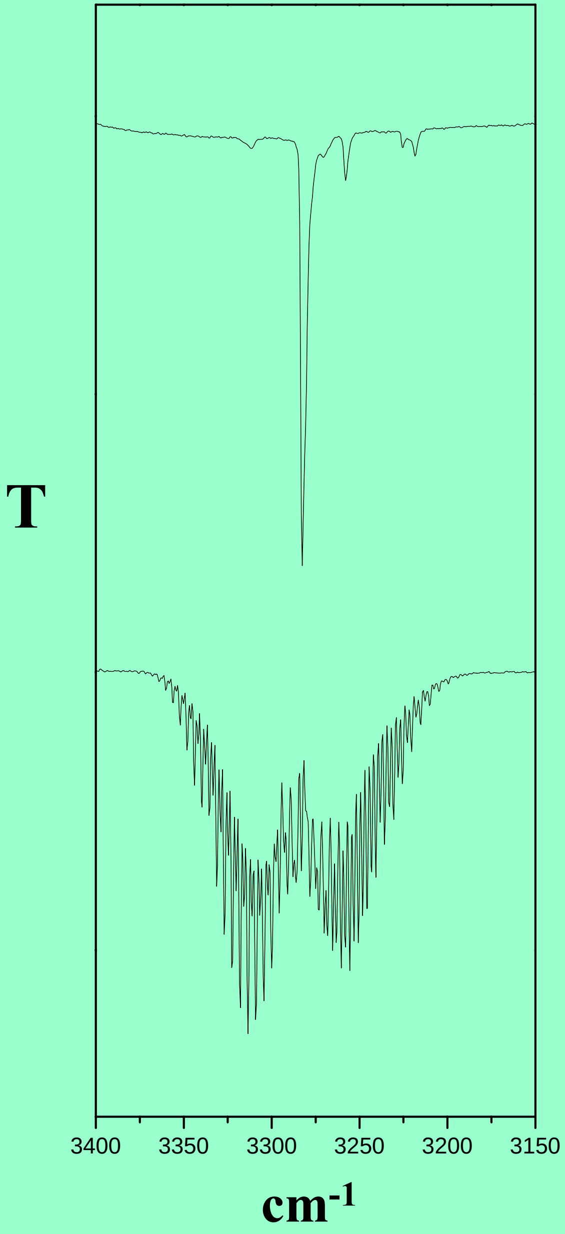


PICTURE OF MOLECULAR ARRANGEMENT

MATRIX ISOLATED **UNISOLATED**



INFRA RED SPECTRA OF ACETYLENE



Matrix isolated C_2H_2 (in Argon)

Gas phase C_2H_2

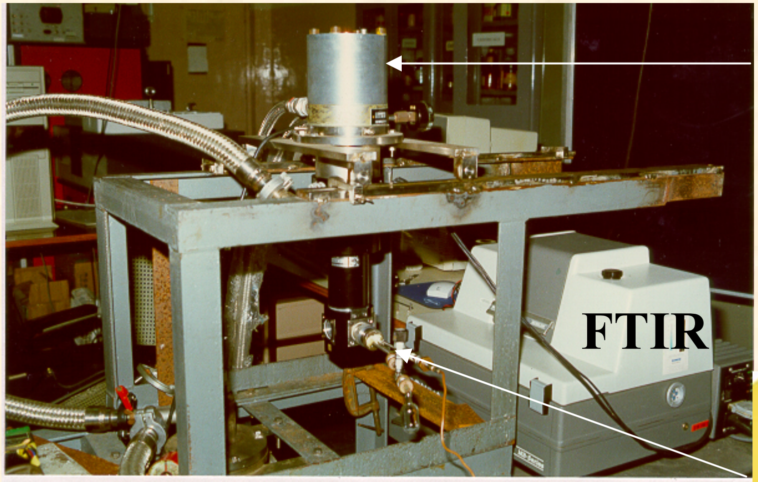
Smaller linewidths

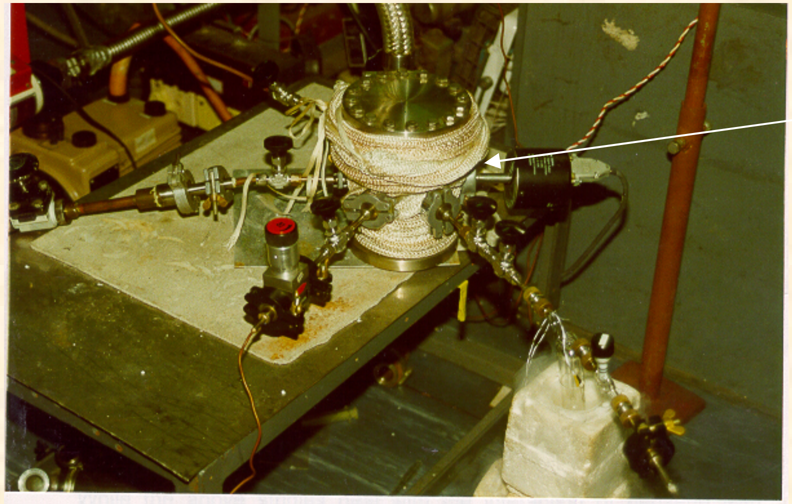
Rovibronic population confined to just a few levels - Low Temperature

Reduced intermolecular interactions

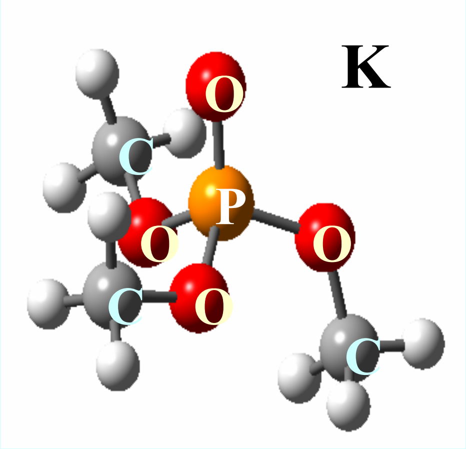
Doppler broadening X

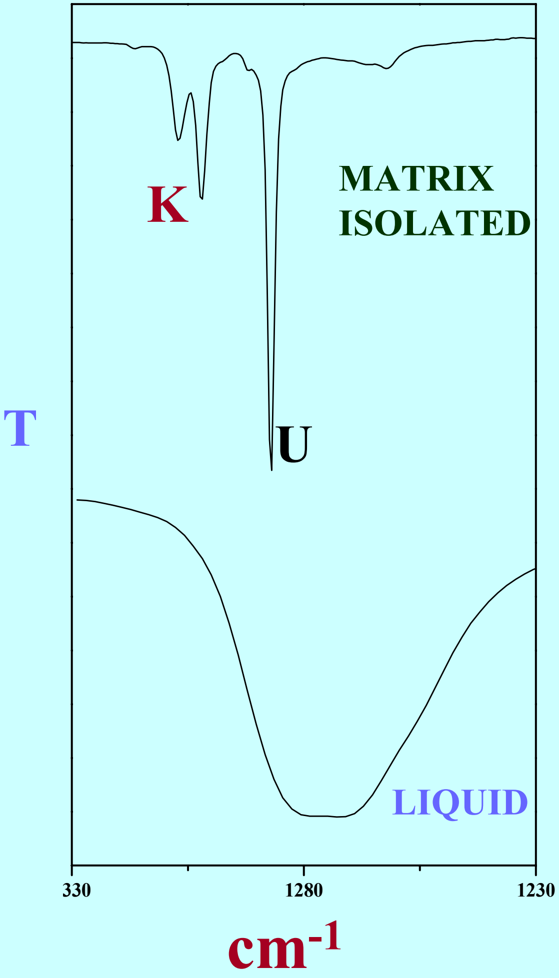
MATRIX ISOLATION IR SET UP

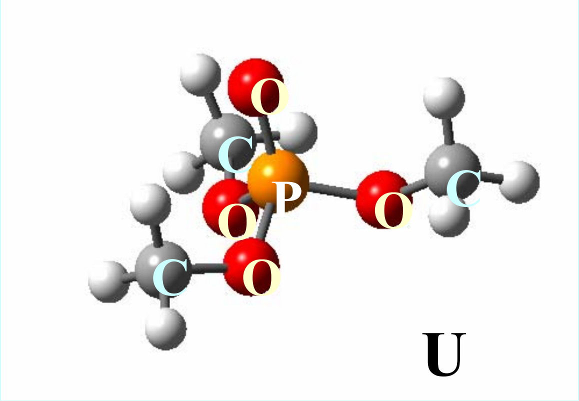




INFRA RED SPECTRA OF TMP







POPULATION PROBLEM!

CONFORMATION 'K'

$\Delta E = 0.5$ kcal/mol

CONFORMATION 'U'

AT T = 300 K $N_K/N_U = 0.2$

AT T = 10 K $N_K/N_U = 10^{-8}$

AT 10K, WE SHOULD THEREFORE NOT SEE THE 'K' FORM

BUT BOTH CONFORMERS ARE SEEN!!!???

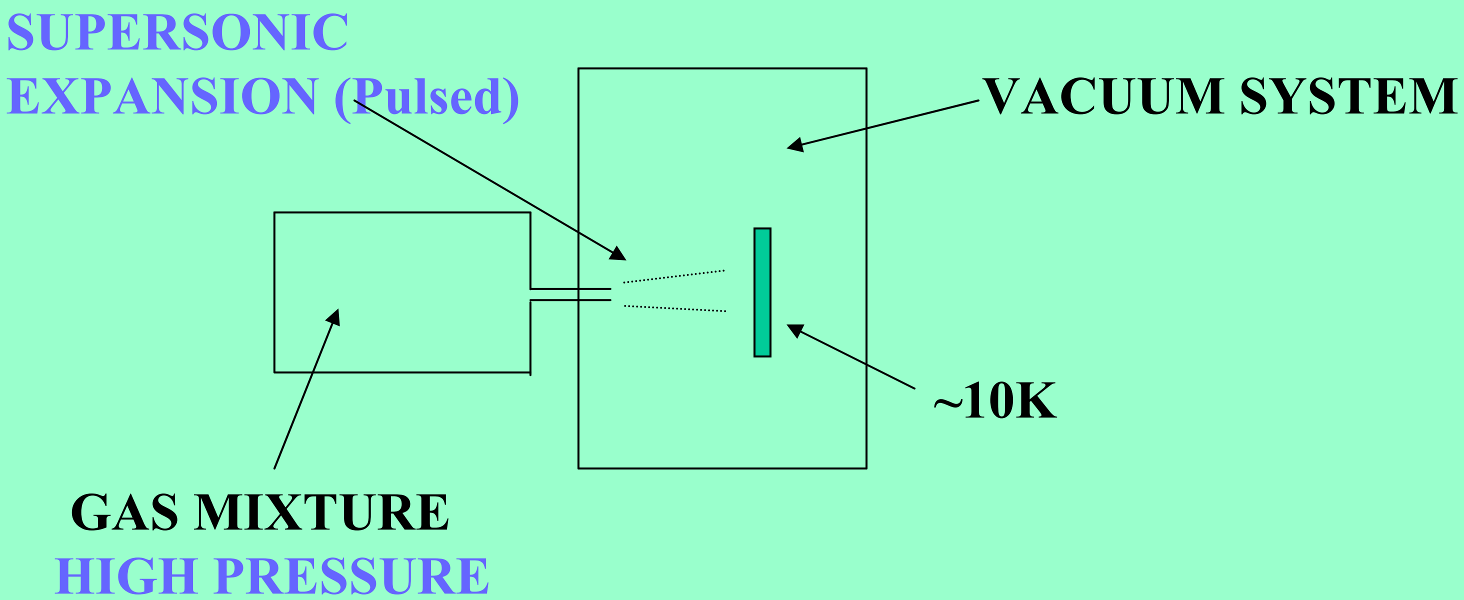
REASON

ROOM TEMPERATURE POPULATION FROZEN IN THE MATRIX

CAGE BARRIER PREVENTS INTERCONVERSION

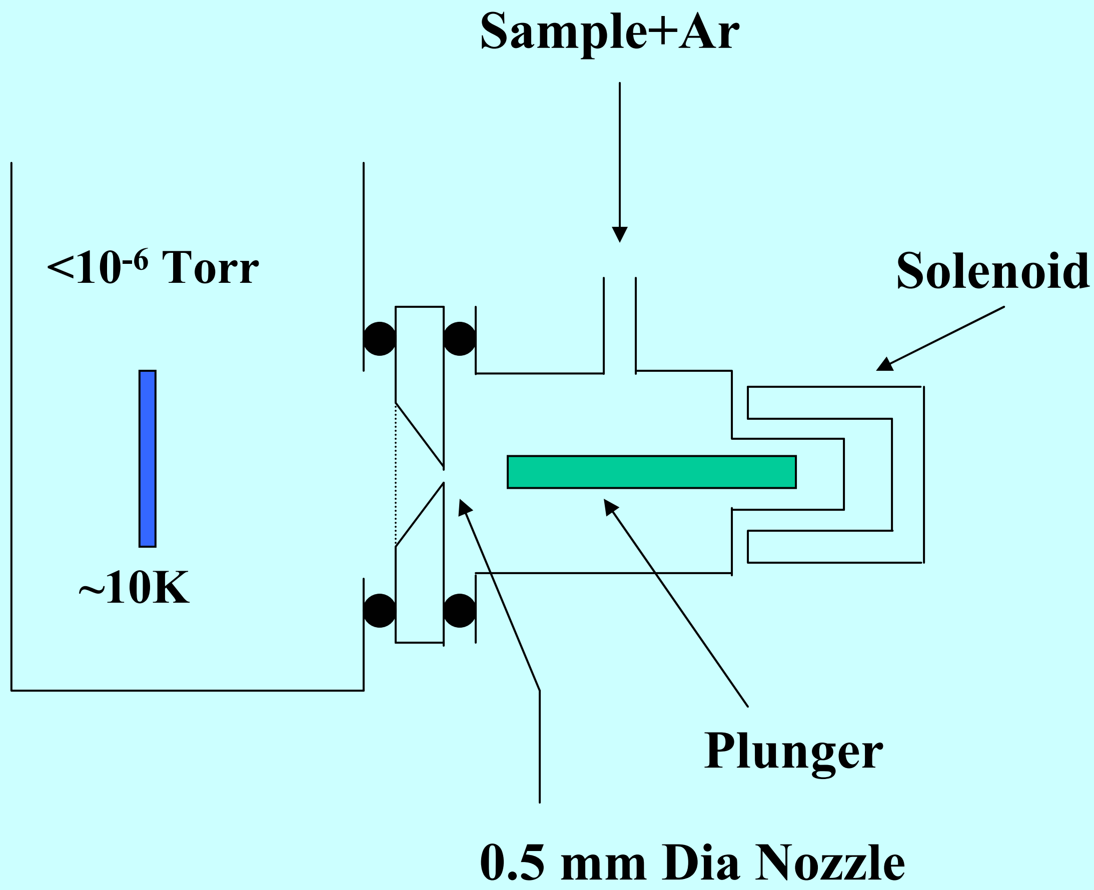
HOW ABOUT COOLING THE MOLECULES IN THE GAS PHASE WHERE NO CAGE EFFECT OPERATES

SUPERSONIC EXPANSION-MATRIX ISOLATION

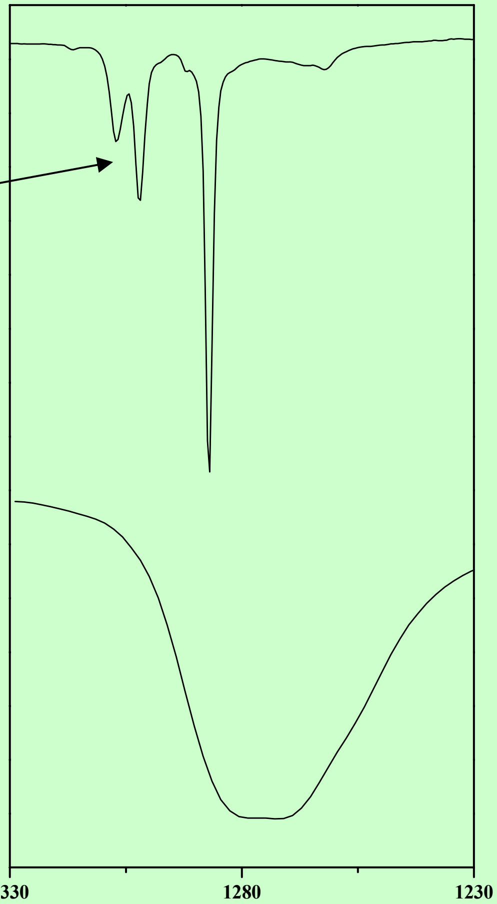


THIS CAGE EFFECT TURNS OUT TO BE QUITE HELPFUL WHEN STUDYING WEAK INTERACTIONS

PULSED SUPERSONIC NOZZLE SOURCE FOR MI



When a supersonic jet source was to deposit the matrix



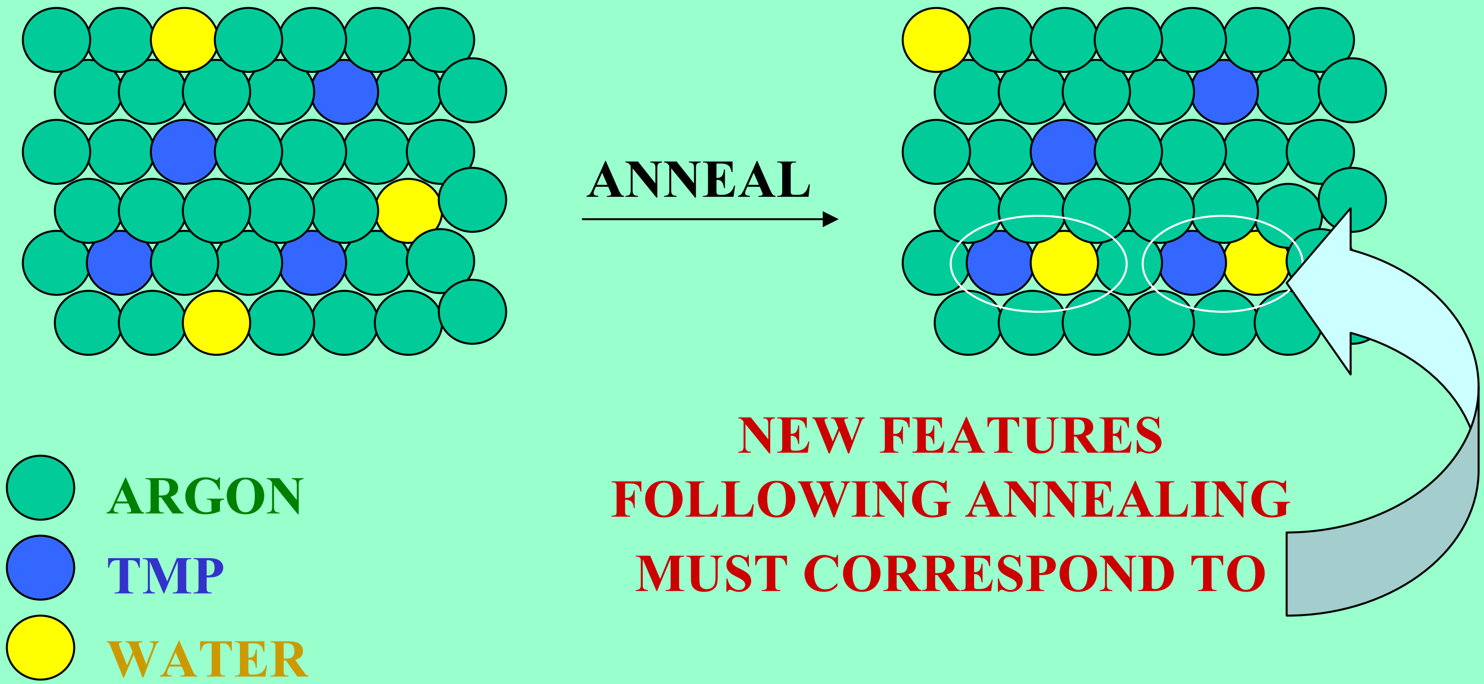
This peak was shown to deplete in intensity

Indicating that the peak must be due to the higher energy conformer

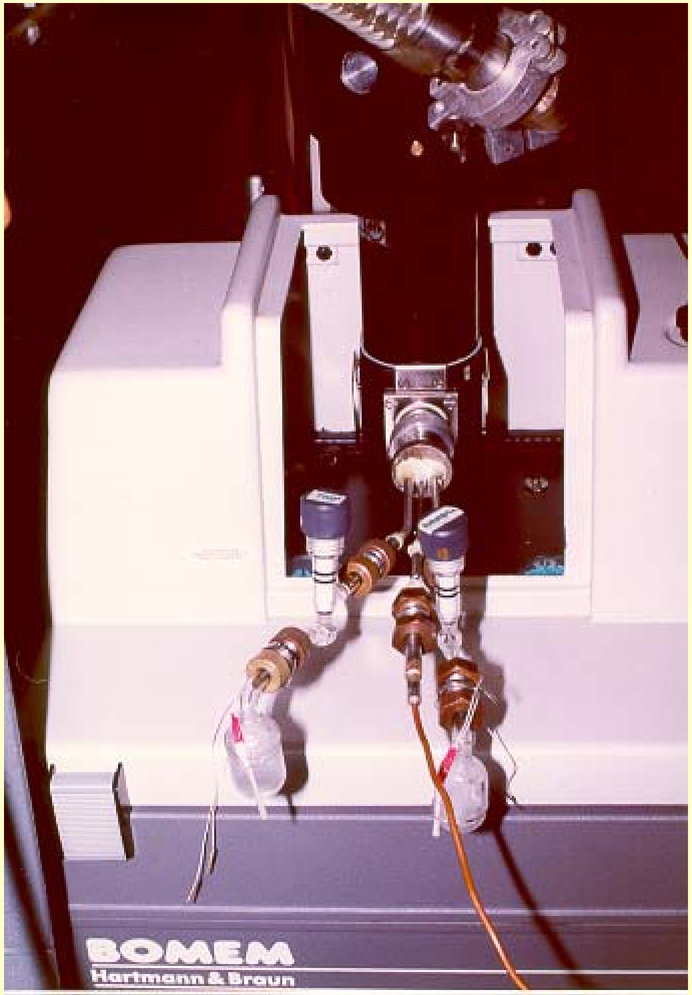
The combination of effusive and supersonic sources are therefore effective when doing matrix isolation spectroscopy

INTERMOLECULAR INTERACTIONS USING MATRIX ISOLATION SPECTROSCOPY

STUDIES OF WEAK INTERACTIONS – HYDROGEN BONDED, VAN DER WAALS



CODEPOSITION NOZZLE

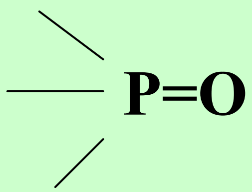


HOW DO YOU KNOW A COMPLEX IS FORMED?

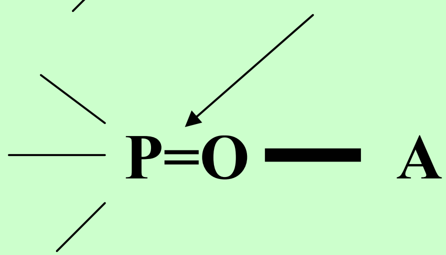
- * NEW FEATURES SEEN <u>ONLY</u> WHEN BOTH REAGENTS ARE CODEPOSITED

- * INTENSITY OF THE NEW FEATURES INCREASE WHEN CONCENTRATIONS OF EACH REAGENT IS INCREASED

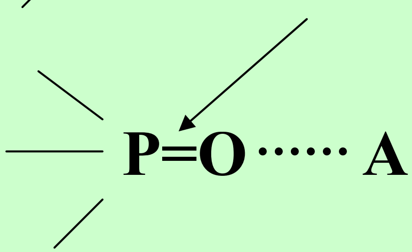
<u>WHAT ABOUT THE STRENGTH OF THE INTERACTION?</u>



1280 cm^{-1}

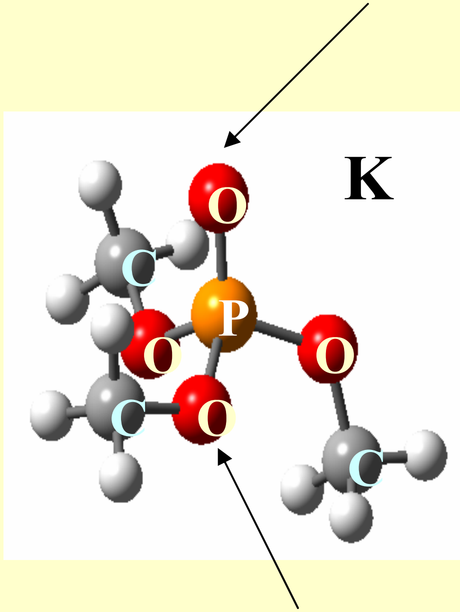


Strong interaction - large shift

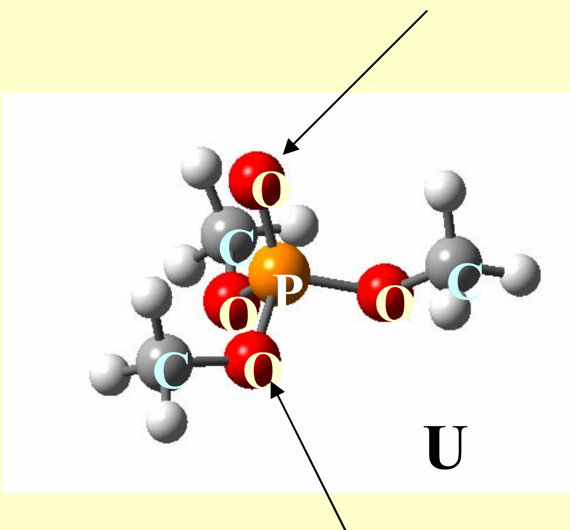


Weak interaction - small shift

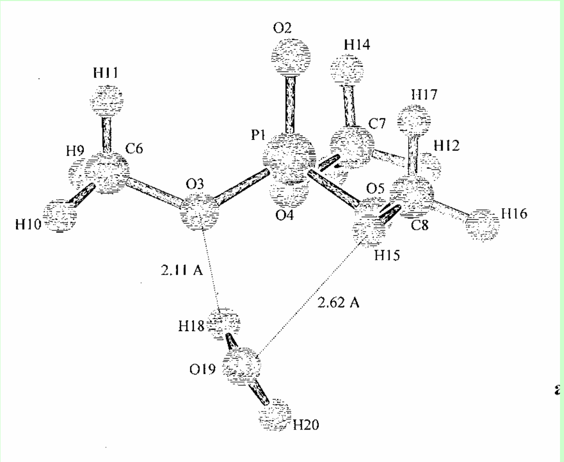
TMP-H_2O INTERACTION



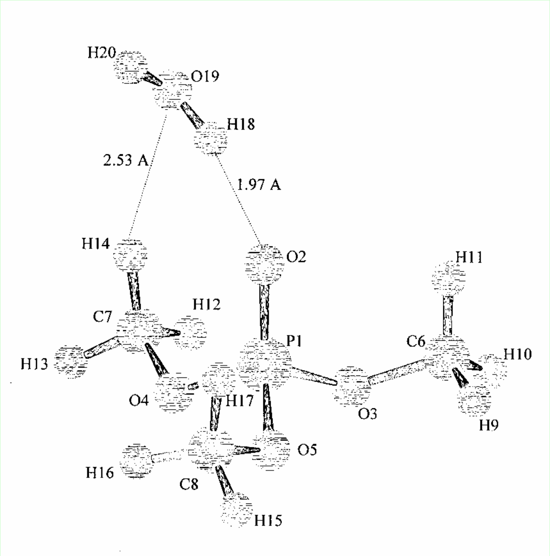
H_2O



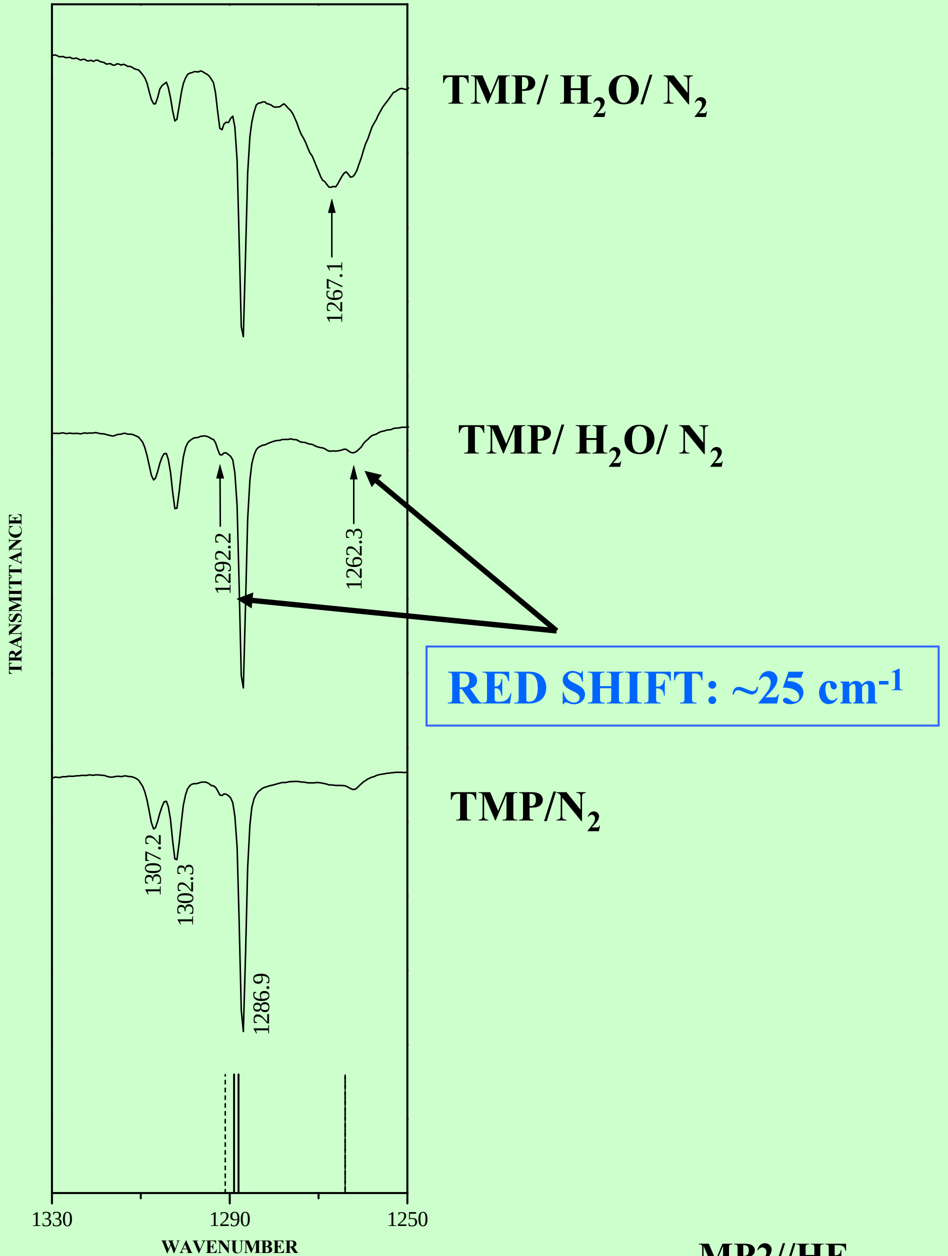
TMP-H_2O INTERACTION



E_s = 10.9 kJ/mol



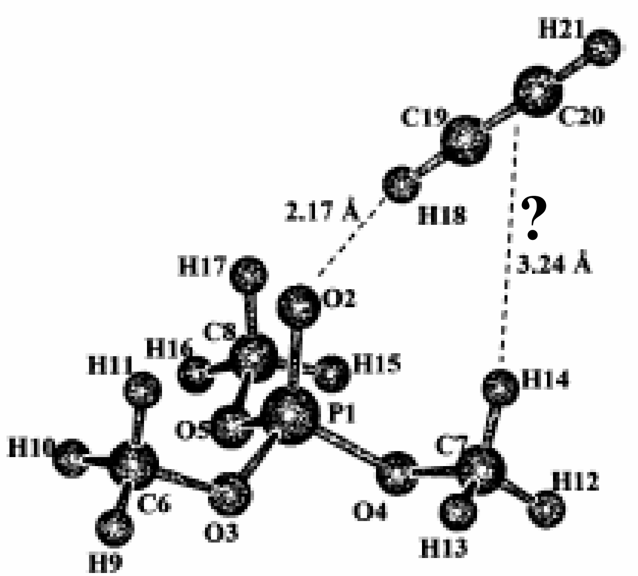
E_s =20.5 kJ/mol

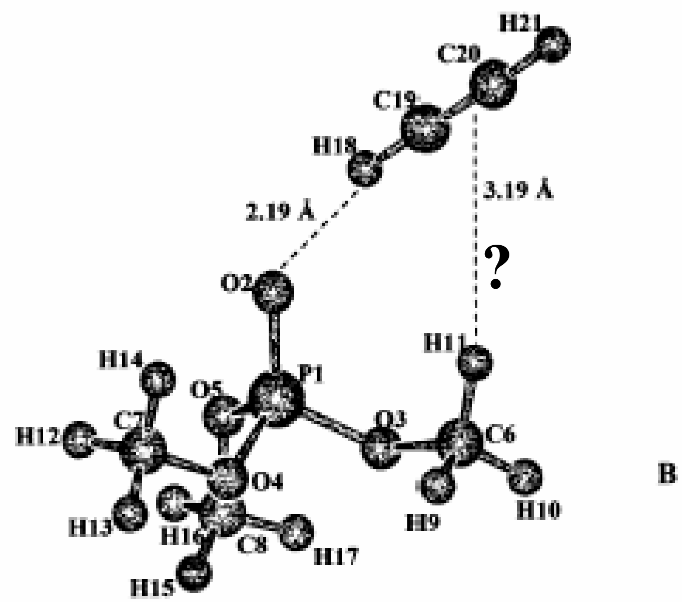


MP2//HF

TMP-ACETYLENE COMPLEX

H-bonds with the phosphoryl oxygen



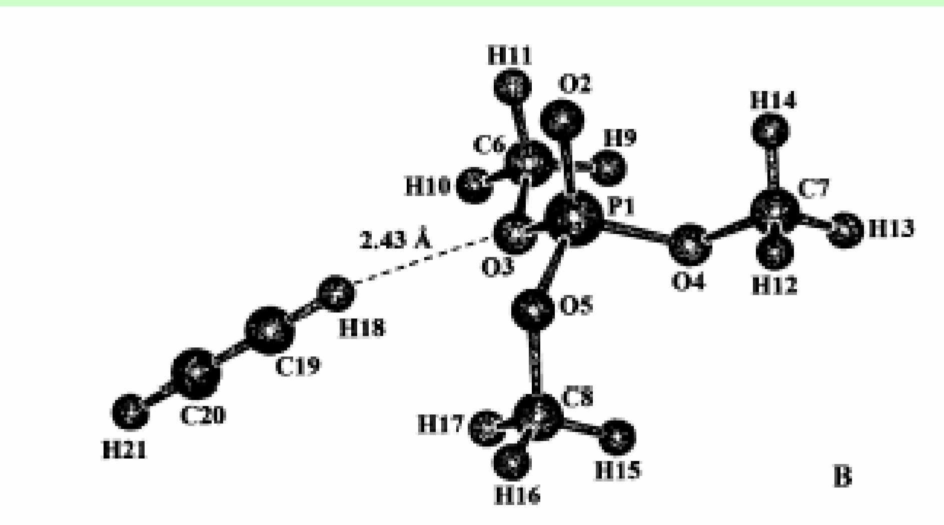


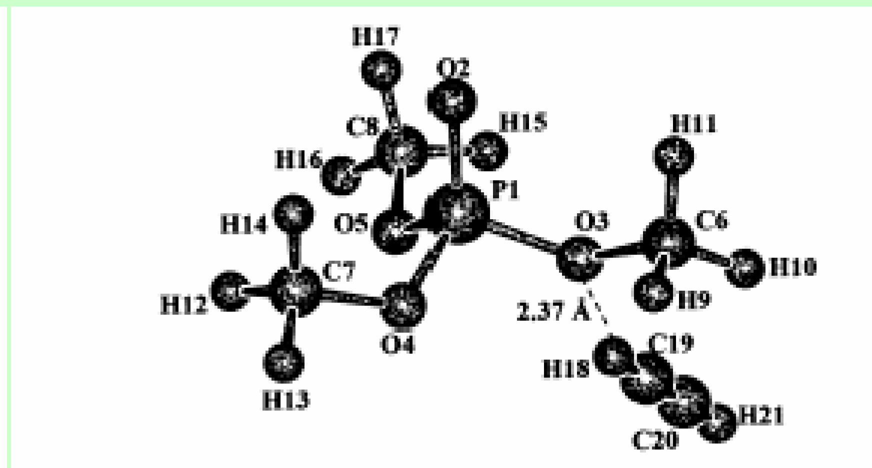
Stabilization energy **15.9 kJ/mol** **15.9 kJ/mol**

HF/6-31G**

TMP-ACETYLENE COMPLEX

H-bonds with the alkoxy oxygen

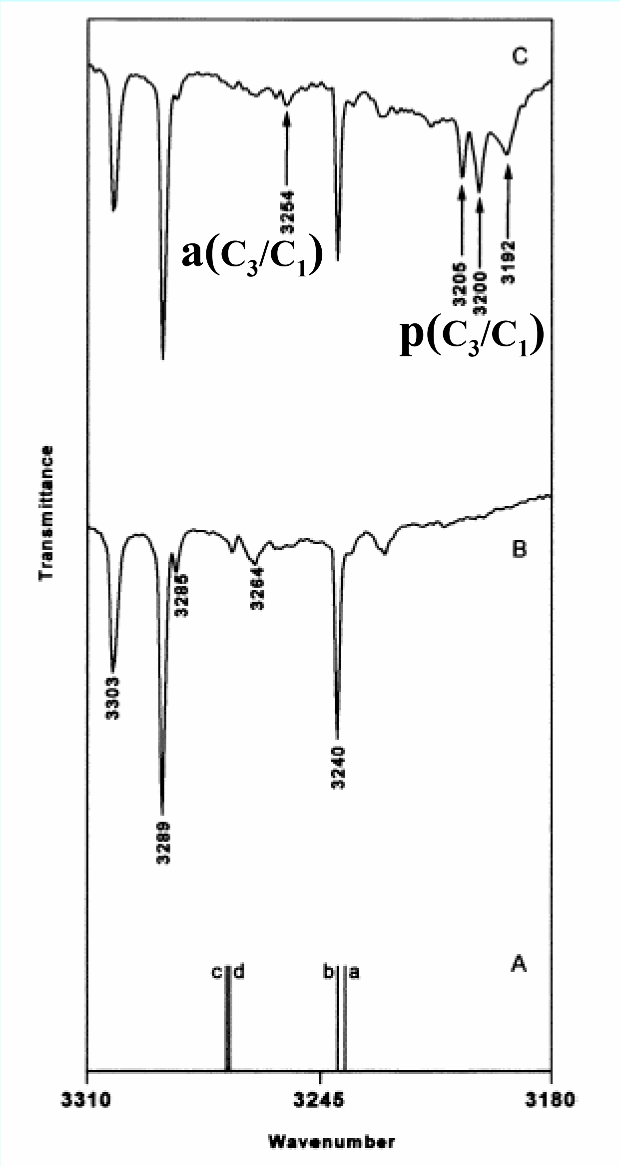


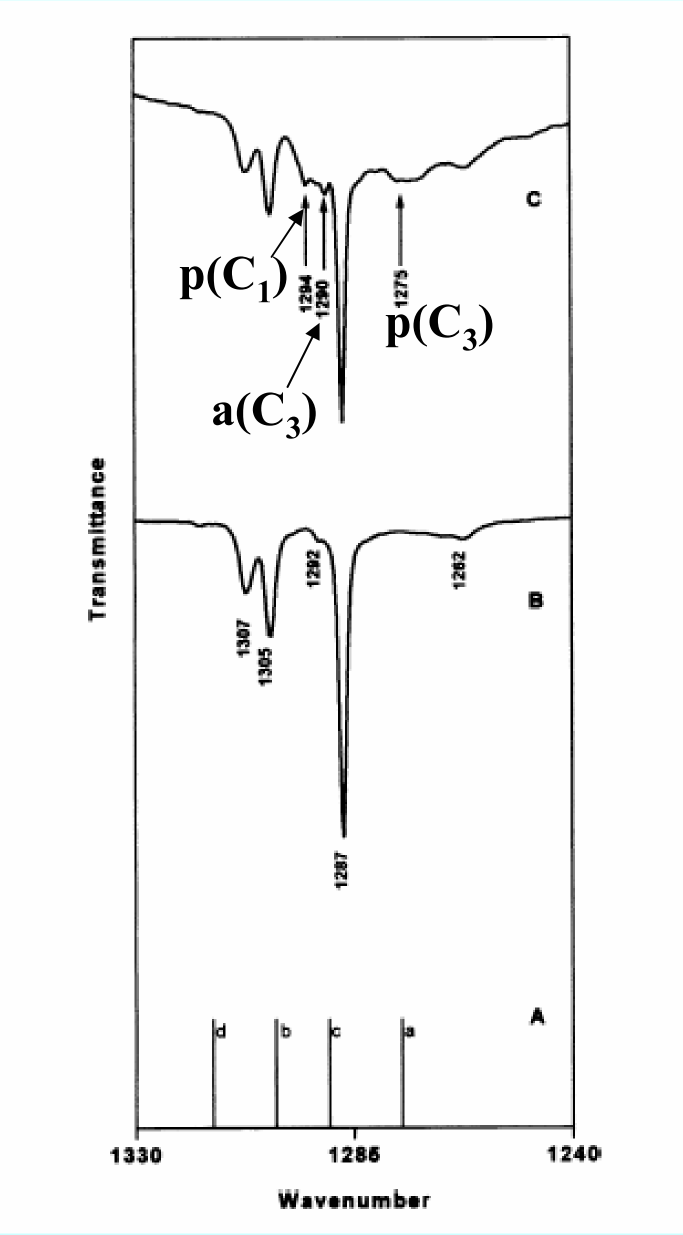


Stabilization energy **7.1 kJ/mol** **7.5 kJ/mol**

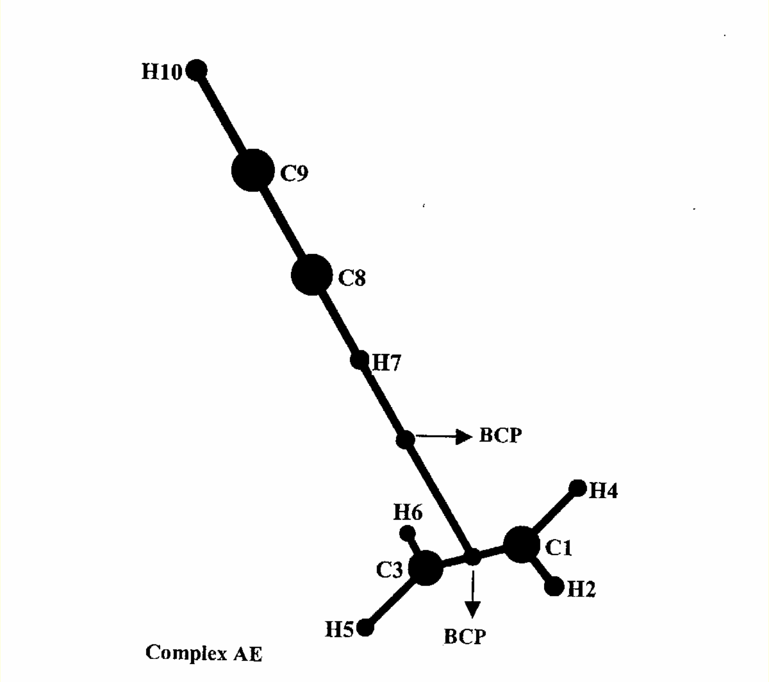
HF/6-31G**

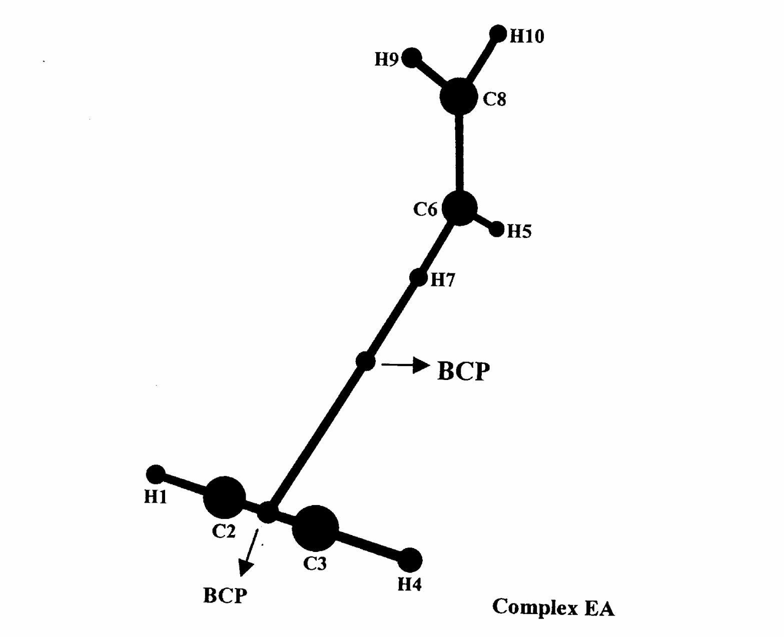
TMP-ACETYLENE COMPLEX





ACETYLENE-ETHYLENE COMPLEX





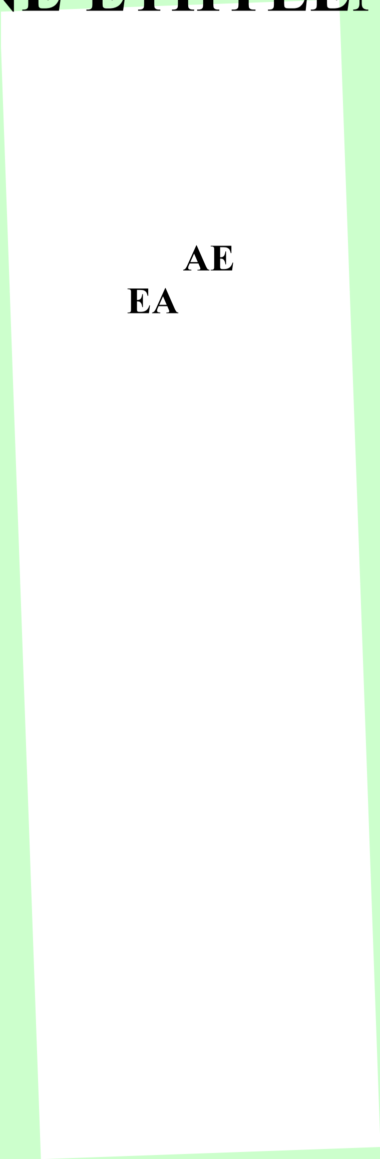
Es = 7.4 kJ/mol

Es = 4.4 kJ/mol

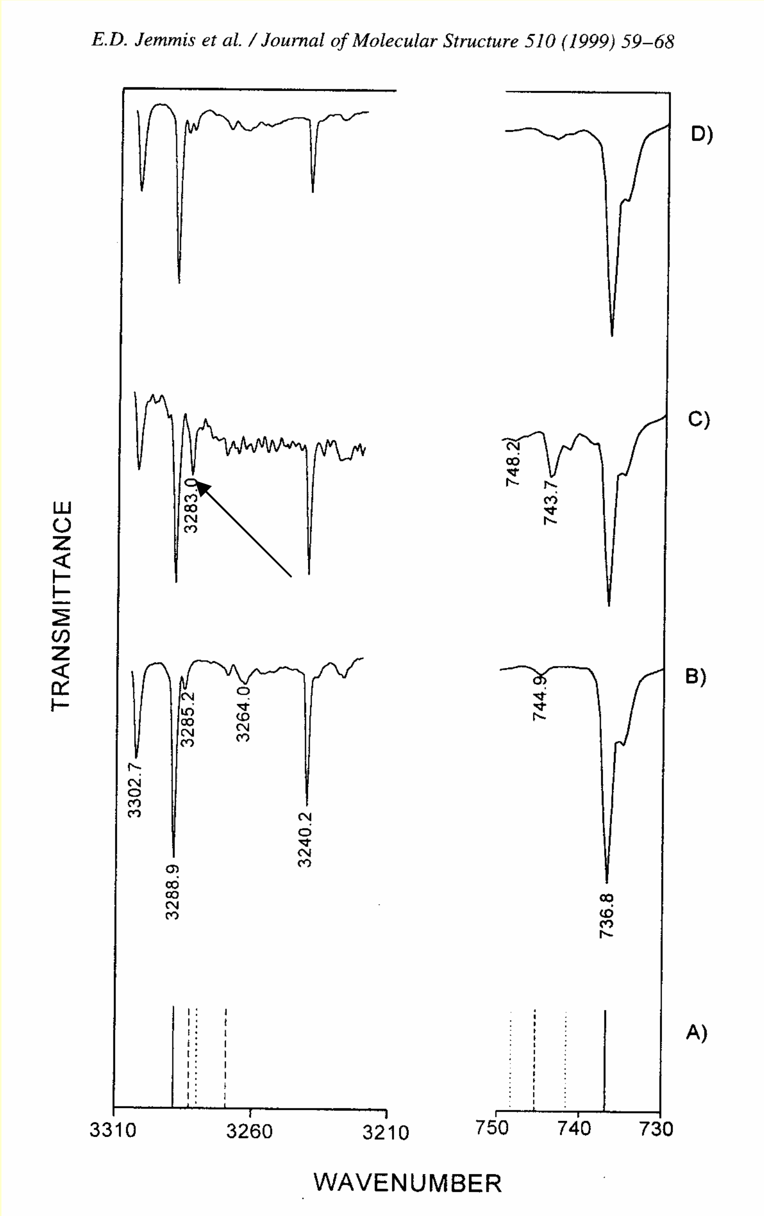
MP2/6-311++G(2d,2p)

Collaboration with Prof. Gadre

ACETYLENE-ETHYLENE COMPLEX

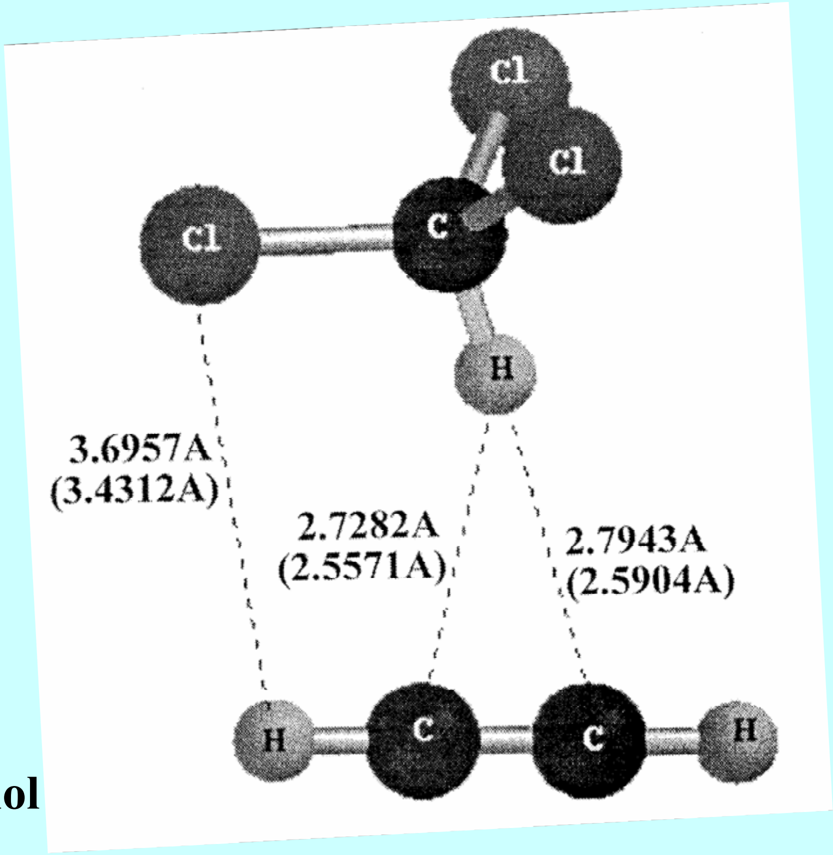


ACETYLENE-CHLOROFORM COMPLEX



Collaboration with Prof. Jemmis

ACETYLENE-CHLOROFORM COMPLEX



Es = 6.4 kJ/mol

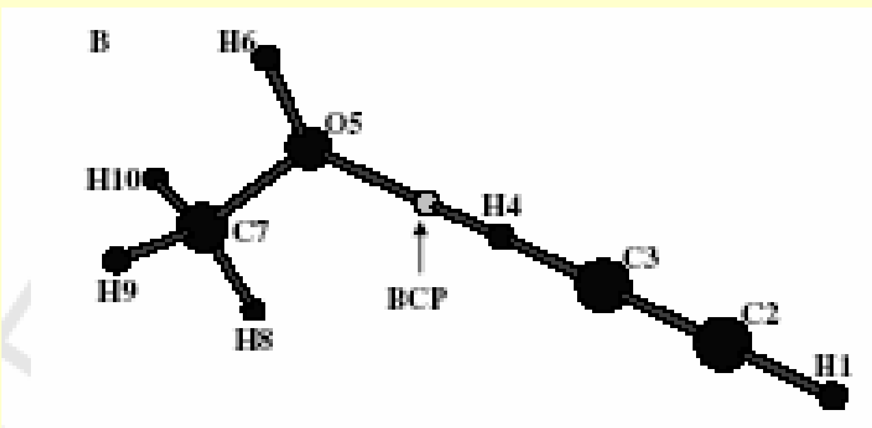
Collaboration with Prof. Jemmis

MP2/6-311++G(d,p)

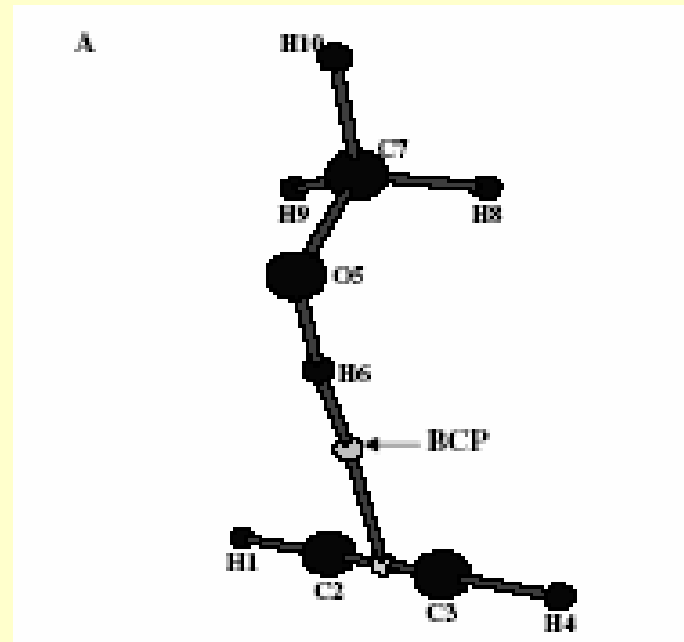
ACETYLENE-METHANOL COMPLEX

Es = 7.7 kJ/mol

Es = 11.8 kJ/mol



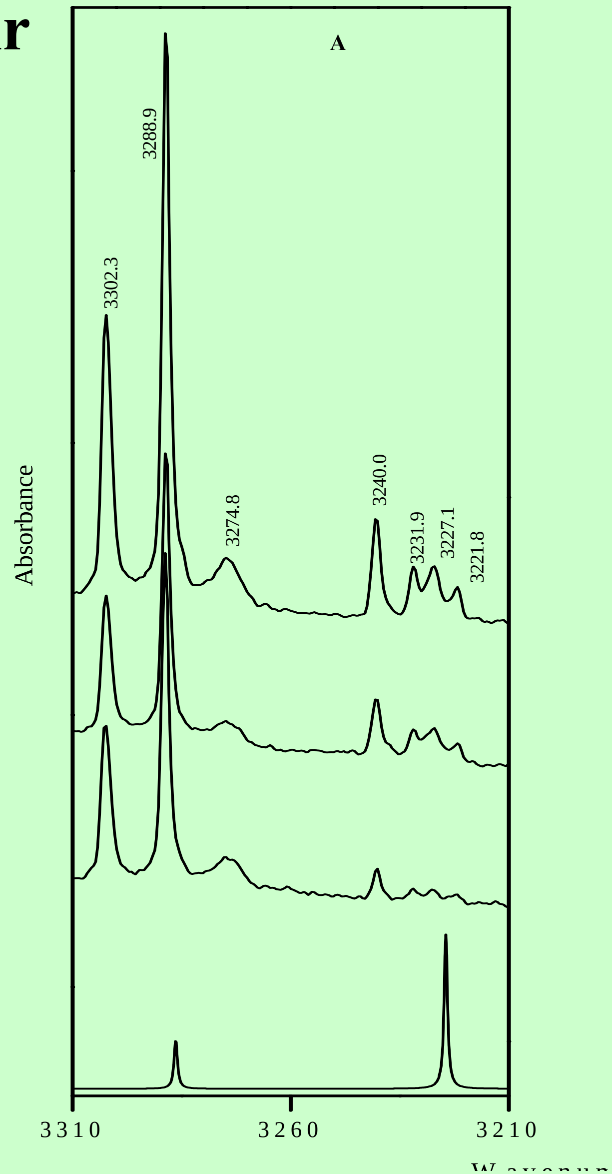
AM complex

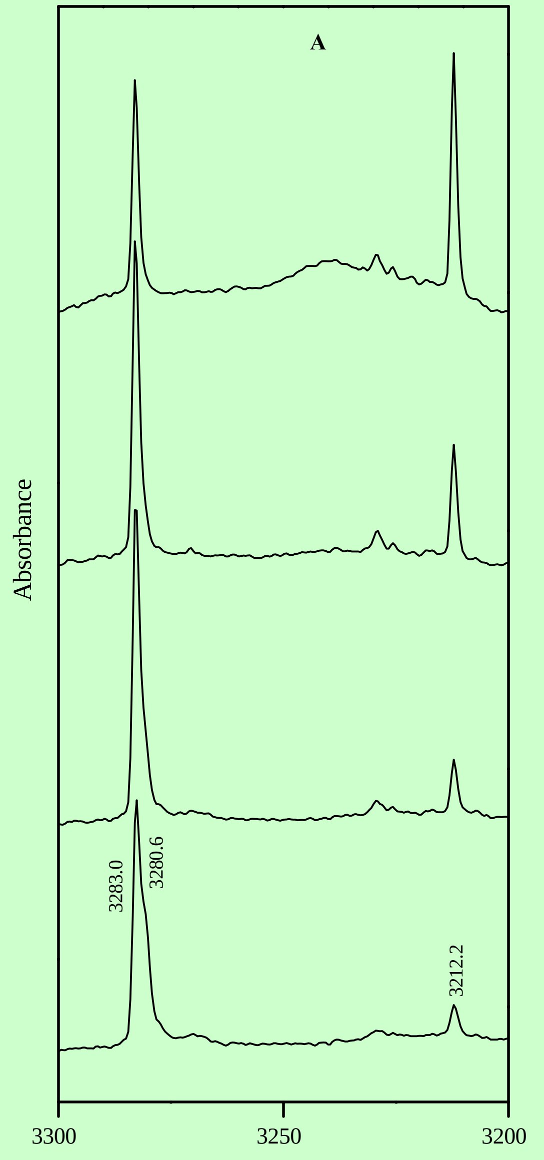


MA complex (H-π)

ACETYLENE-METHANOL COMPLEX

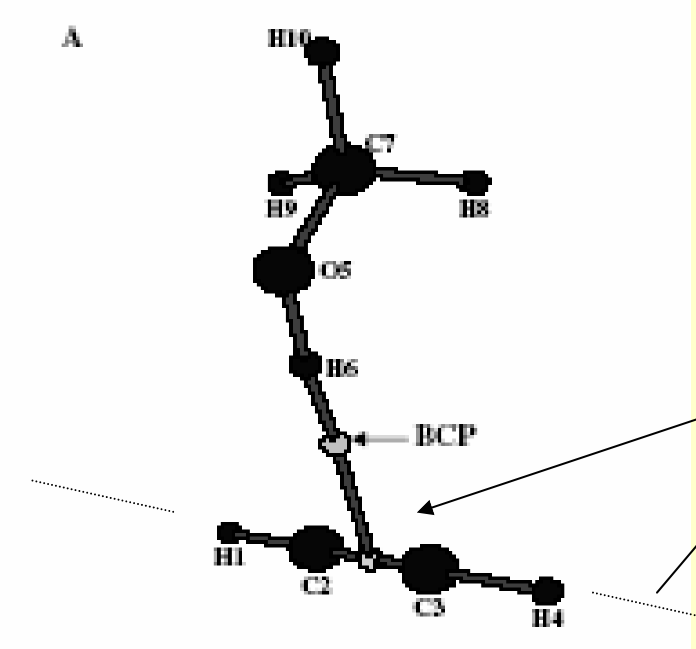
Ar





N_2

Role of the matrix in stabilizing very weak interactions



N_2

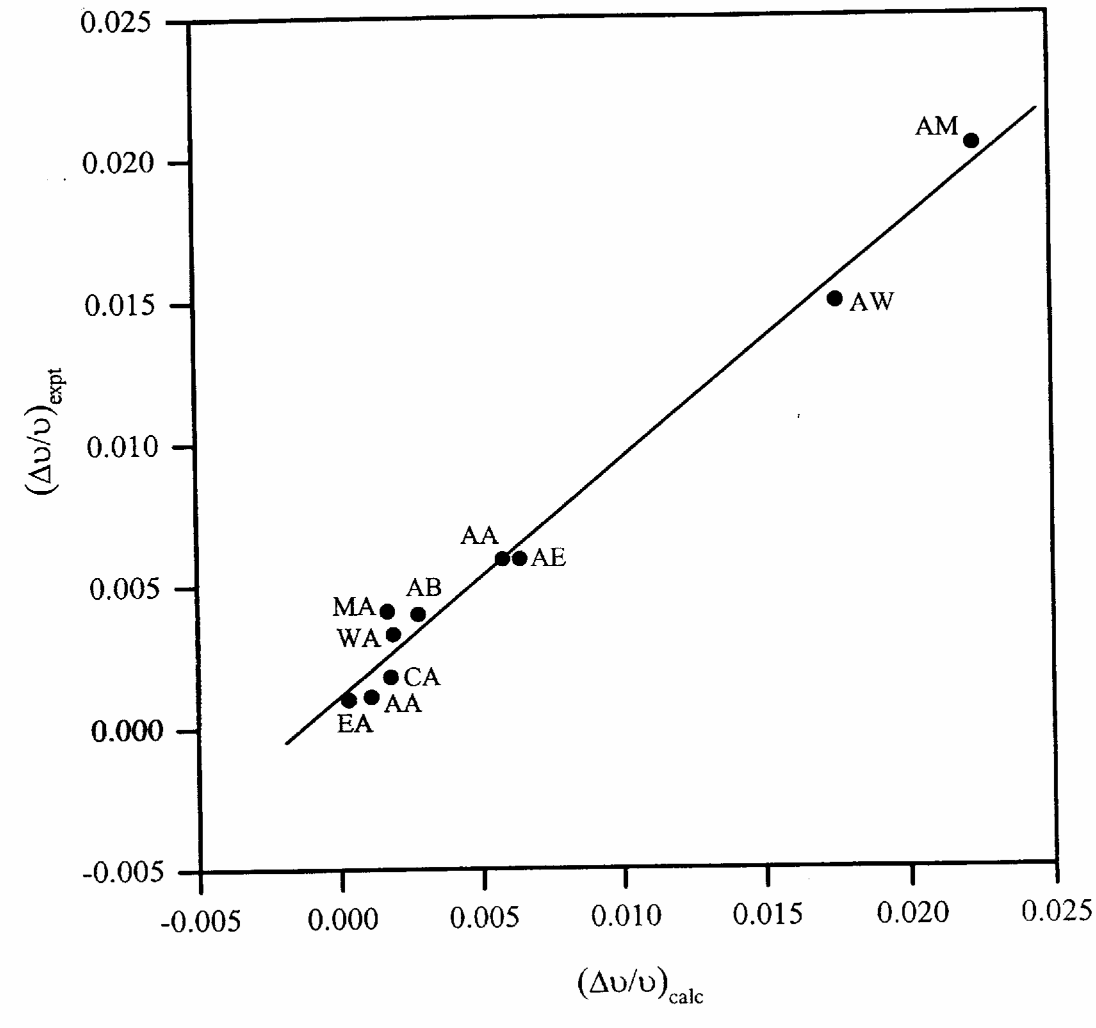
Increase in basicity

N_2

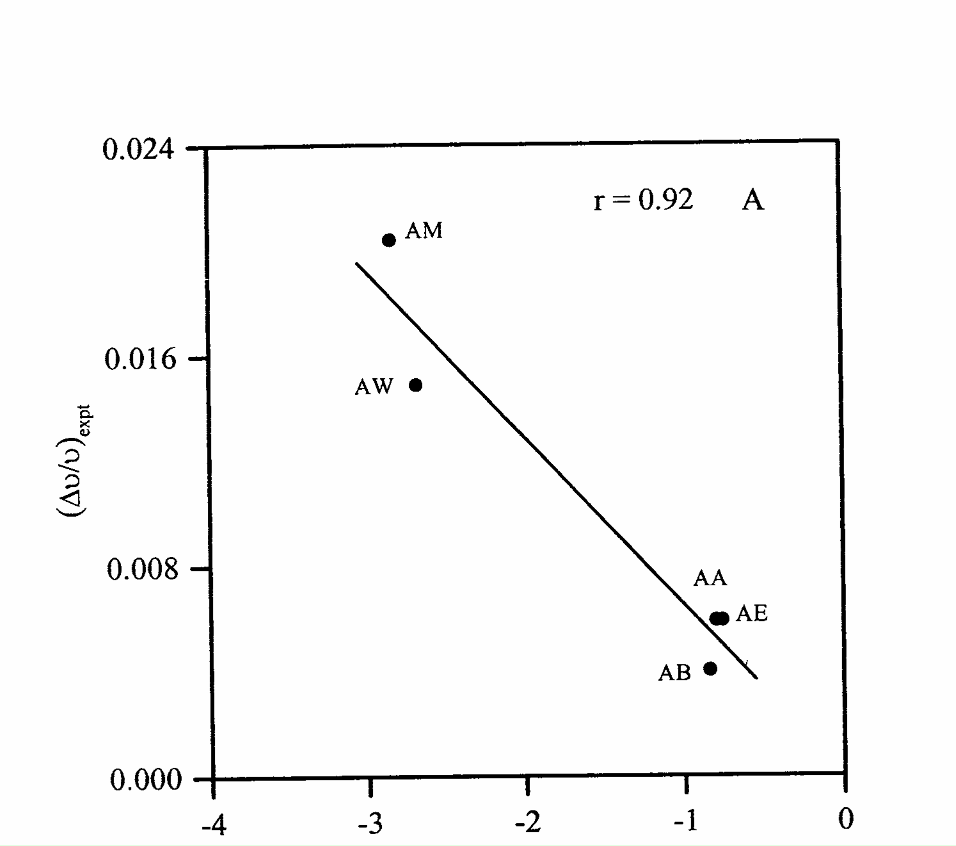
N_2

Collaboration with Prof. Gadre

Experimental Vs Computed Shifts in Vibrational Frequencies



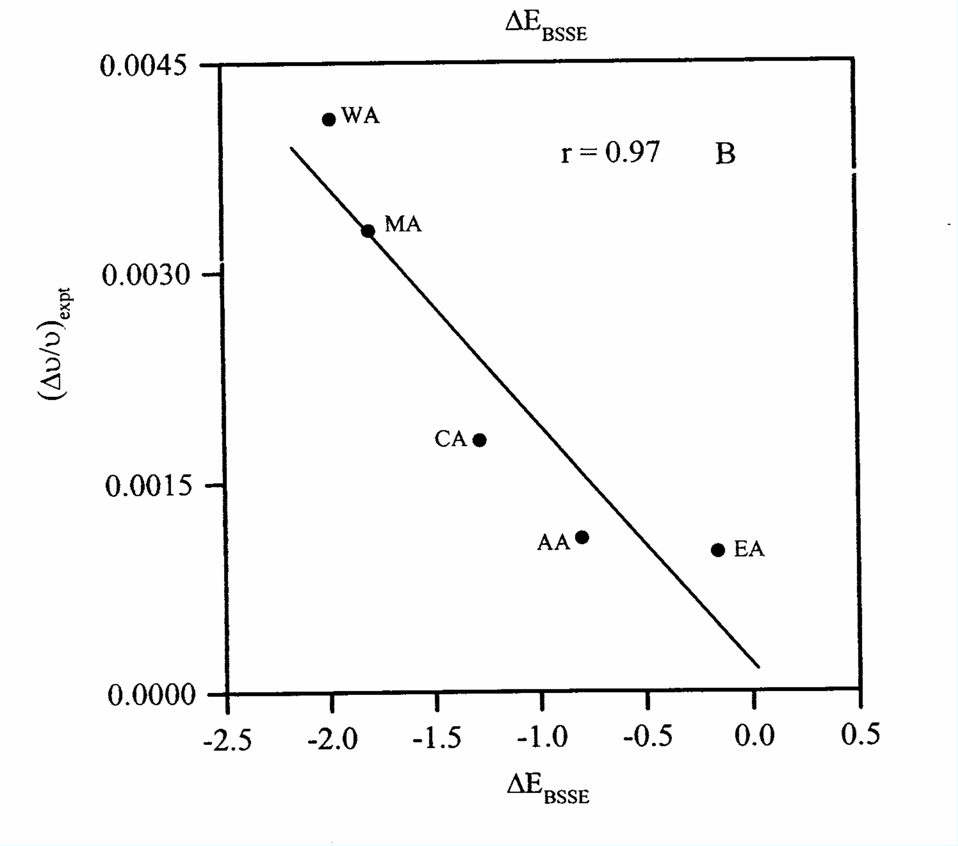
Experimental shifts Vs Computed Stabilization energies



ΔE_{BSSE}

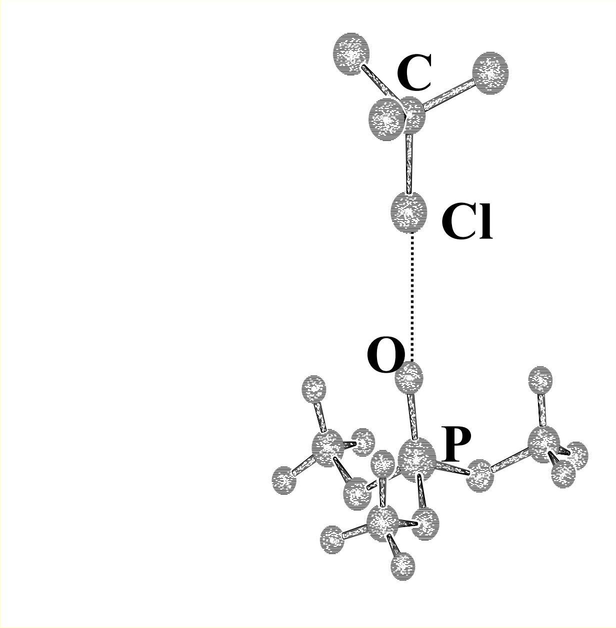
Complexes where C_2H_2 is the proton donor

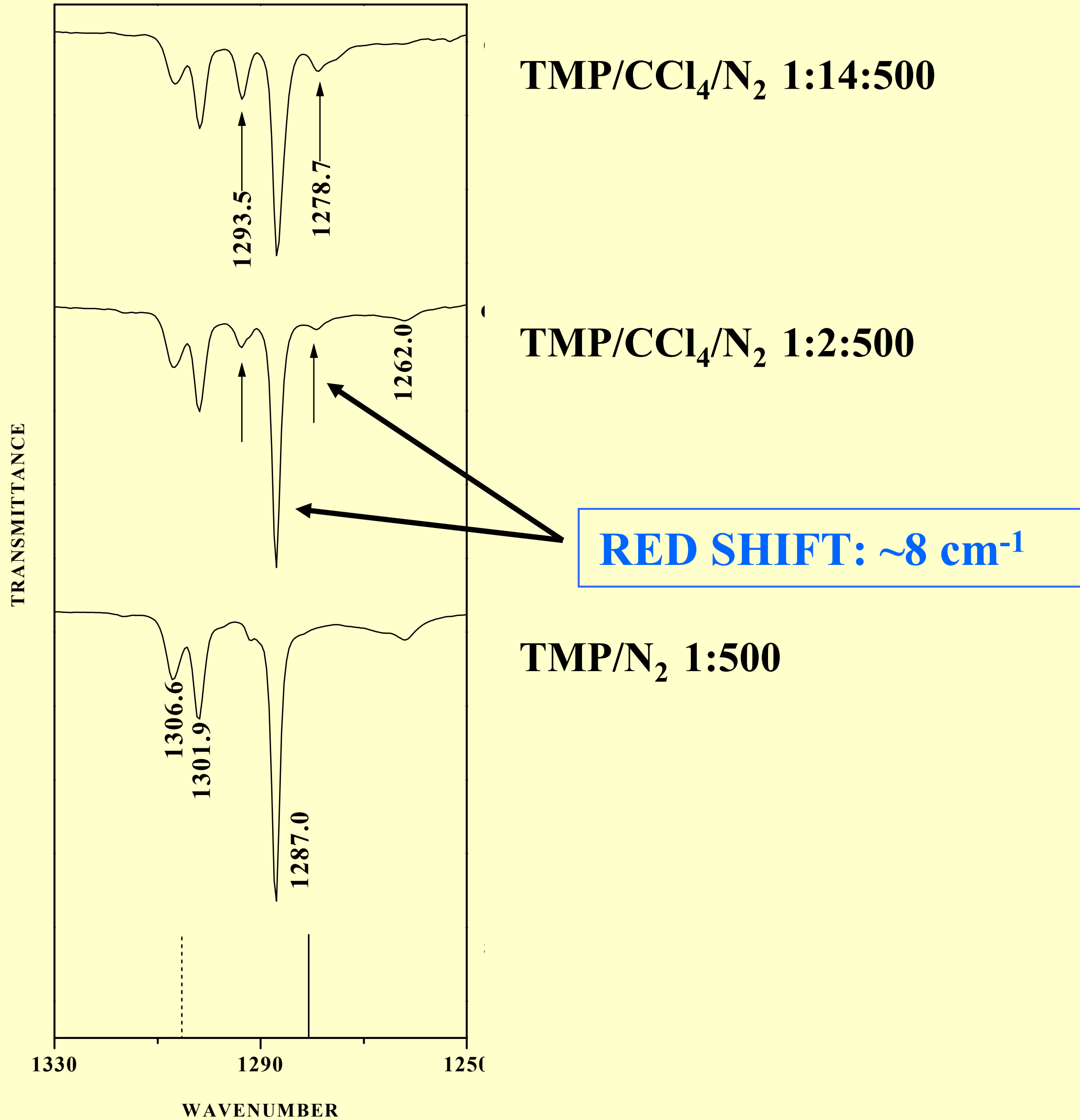
Experimental shifts Vs Computed Stabilization energies



Complexes where C_2H_2 is the proton acceptor

TMP-CCl_4 INTERACTION





MATRIX ISOLATION

MOLECULAR STRUCTURES

WEAK COMPLEXES

Trapped in their minimum and unable to transform to a more stable minimum

The matrix aids in stabilizing this minimum by altering the basicity (or acidity) of the reagent

Such complexes would probably not be observed in gas phase studies where interconversion would be possible.

Certainly such weak complexes would elude conventional room temperature studies

The Group

Lisa George

Sankaran

Vidya

Sundararajan

Thank You

TMP-H_2O INTERACTION