The Long and Short of Weak Hydrogen Bonds

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Hydrogen Bond (HB)

X-H……Y

HB Donor **HB Acceptor**

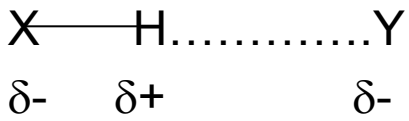
Usually electronegativity of X > H
And Y is rich in electron density

Bond strength ~40 kcal/mol and below.

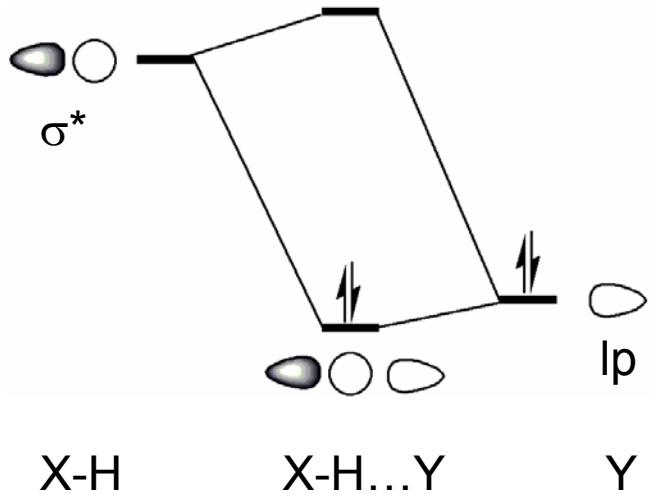
Weakest in the range of 4 kcal/ mol and below

Standard Explanation

Electrostatic:



Covalent: Negative Hyperconjugation



Manifestation of HB

Lengthening and Weakening of X-H bond
Red shift of X-H stretching mode
Increase of Intensity of X-H stretching mode in IR spectrum
Lower the redshift, weaker the H-Bond

Lengthening and Weakening of X-H bond
Red shift of X-H stretching mode
Increase of Intensity of X-H stretching mode in IR spectrum

Weaker the H-Bond, Lower the redshift
minimal lengthening of X-H bond

Shortening of X-H bond and
blue-shift in in X-H frequency is counter-intuitive
even for the weakest of H-Bonds

Yet many examples are now known where

Shortening and Strengthening of X-H bond
Blue shift of X-H stretching mode
Decrease of Intensity of X-H stretching mode in IR spectrum

How do we understand the reversal?

H_3C-H…OH_2

H_2C=CH-H…OH_2

F_3C-H….C_6H_6

C_6H_5-H…C_6H_6

F_3Si-H…NH_3

F_4P-H....FH

F_2N-H…FH

F-Kr-H…CO

Plan of the talk

How we got interested in the problem

Review of explanations available

Detailed analysis of PES

Electron Density Shifts

Generalizations

Acknowledgements

How we got interested in the problem

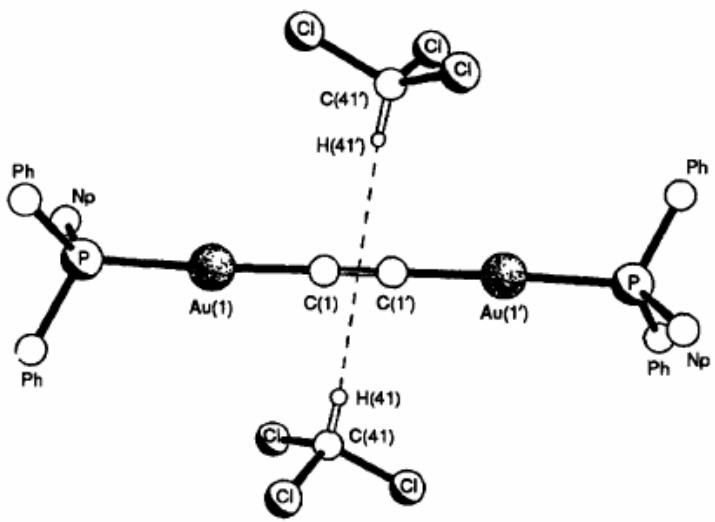


Fig. 1 The C–H···π interactions in **1**

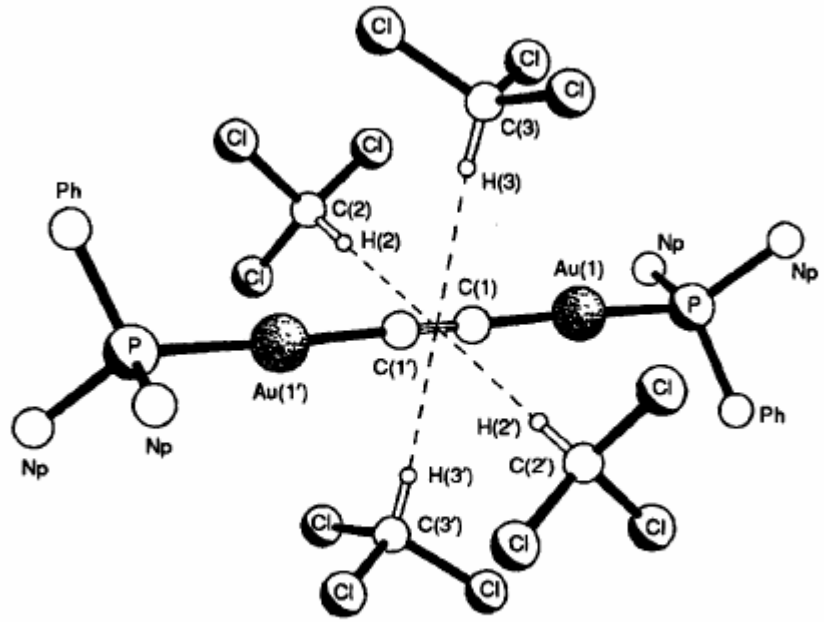
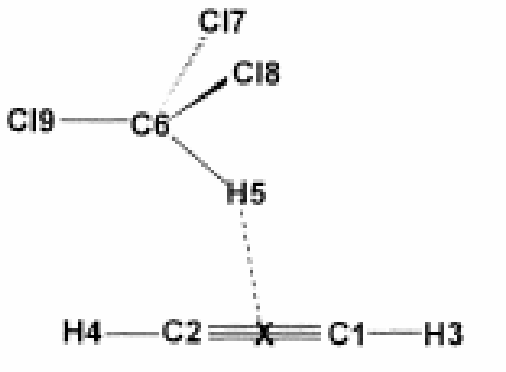


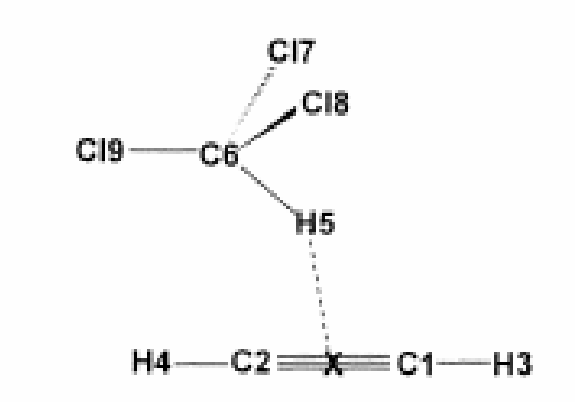
Fig. 2 Pseudo-octahedral arrangement of $CHCl_3$ around the C(1)≡C(1′) ethyne bond in **2**, showing the C–H···π interactions

Mingos, D. M. P et al. *J. Chem. Soc., Chem. Commun,* ***1994****, 1787*



Parameter	MP2/6-311+G(d,p)
C1–H3	1.0658 (1.0645)
C1–C2	1.2175 (1.2162)
C2–H4	1.0660 (1.0645)
C6–H5	1.0836 (1.0848)
C6–Cl7	1.7650 (1.7652)
C6–Cl9	1.7678 (1.7652)
X–H5	2.5010
C1–H5	2.5904
C2–H5	2.5571
C2–C6	3.5147
C2–Cl9	3.7556
H4–C6	3.7123
H4–Cl9	3.4312
∠C2–C1–H3	179.2 (180.0)
∠C2–C1–H4	179.8 (180.0)
∠H5–C6–Cl7	107.8 (107.6)
∠H5–C6–Cl9	107.1 (107.6)
∠Cl7–C6–Cl8	111.4 (111.3)
∠Cl7–C6–Cl9	111.2 (111.3)
∠X–H5–C6	160.6
∠C1–X–H5	91.6
∠C2–X–H5	88.4
∠H3–C1–H5	106.0
∠H4–C2–H5	101.9

All results at MP2/6-311+G(d,p) levels



K. S. Viswanathan 1996

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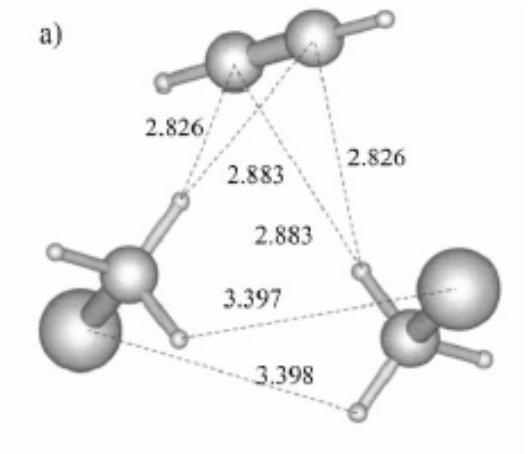
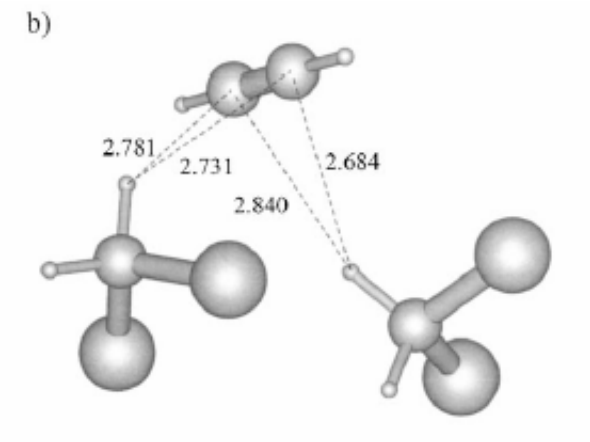
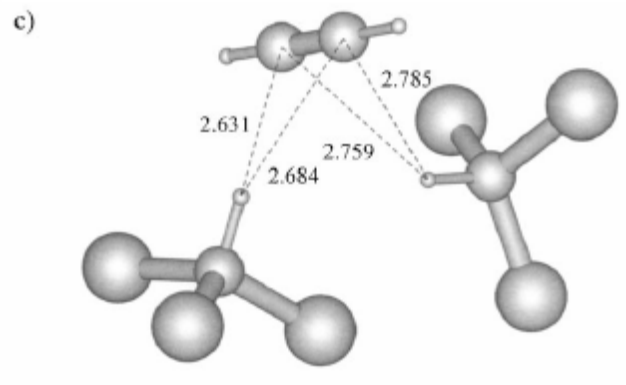
J. Mol. Str. 1999, 510,59



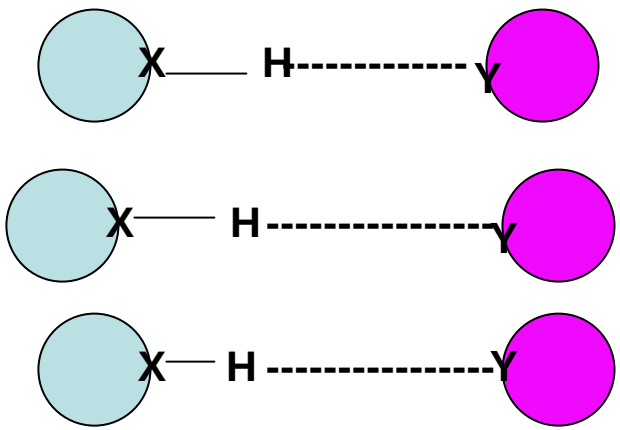




SCF	**-0.23**	**-0.69**	**-0.69**
MP2	**-1.44 (-1.57+0.14)**	**-1.86 (-1.06-0.80)**	**-2.31 (-0.72-1.59)**
Total	**-1.67**	**-2.55**	**-3.00**

The decrease of the C–H bond lengths of the CH_3Cl, CH_2Cl_2 and $CHCl_3$ in the complexes considered here in relation to the isolated molecules is in tune with the theoretical and experimental result on the 1:1 $CHCl_3$-acetylene complex [16]. Such decrease of the C–H bond length on formation of the C–H…π bond has forced the term anti-H-bond in literature [23]. The decrease in the C–H bond length is an attempt to increase the dispersion energy by bringing electrons in the two molecules as close as possible. This is to be contrasted with the conventional H-Bond where the interactions are dominated by electrostatics. This is enhanced by the stretching of the X–H bond.

J. Mol. Str. 2000, 556,315.



Final geometry

Some Experimental Results

Experimental wavenumber shifts of ν(CH) and relative intensities (in parentheses) observed for complexes of $HCCl_{3-x}F_x$ with oxygen-containing bases in liquefied rare gases

Base	Solvent	HCF_3	$HCClF_2$	$HCCl_2F$	$HCCl_3$
$(CH_3)_2O$	Ar	+17.7 (0.09)	+14.0 (0.86)	+4.8 (33)	−8.3 (56)
$(CD_3)_2O$	Ar	+18 (0.14)			
$(CD_3)_2CO$	Kr	+26.7 (0.08)	+24.1 (0.61)	+15.5 (3.8)	+0.6 (58)
C_2D_4O	Kr	+24.1 (0.13)	+20.7 (0.48)	+14.2 (4.5)	+1.3 (69)

van der Veken, B. J. *et al. JACS*, ***2001***, *123, 12290.*
JACS, ***2002***, *124, 7490.*
JACS, ***2002***, *124, 11854.*

Some Experimental Results

cation	anion	"a_{1g}" (cm^{-1}) Raman	$\Delta\nu$	"e_{1u}" (cm^{-1}) infrared	$\Delta\nu$
$[FeCp_2]^+$	$[PF_6]^-$	3130	+10	3124	+14
	$[BF_4]^-$	3126	+6	3103	−7
	$[FeCl_4]^-$	3116	−6	3102	−8
	$[SbCl_4]^-$	3114	−4	3103	−7
	$[I_3]^-$	3098	−22	3090	−20
$[CoCp_2]^+$	$[Co(CN)_6]^{3-}$	3135	+11	3128 av	+13 av
	$[PF_6]^-$	3134	+10	3128	+13
	$[Co(CO)_4]^-$	3128	+4	3119	+4
	$[Br_3]^-$	3110	−14	3100	−15
	$[I]^-$	3059	−65	3057	−58

Diana, E; Stanghellini, P. L, *JACS, **2004**, 126, 7418.*

Dispersion Energy and Pauli Repulsion

Dispersion energy (Intermolecular correlation energy) major component in the total Interaction energy of the weak complexes. To increase the dispersion energy, molecules have to come closer and this brings H in Pauli/short range repulsive region, so X-H bond shortens.

Several X-H bond contractions are predicted even at HF theory.

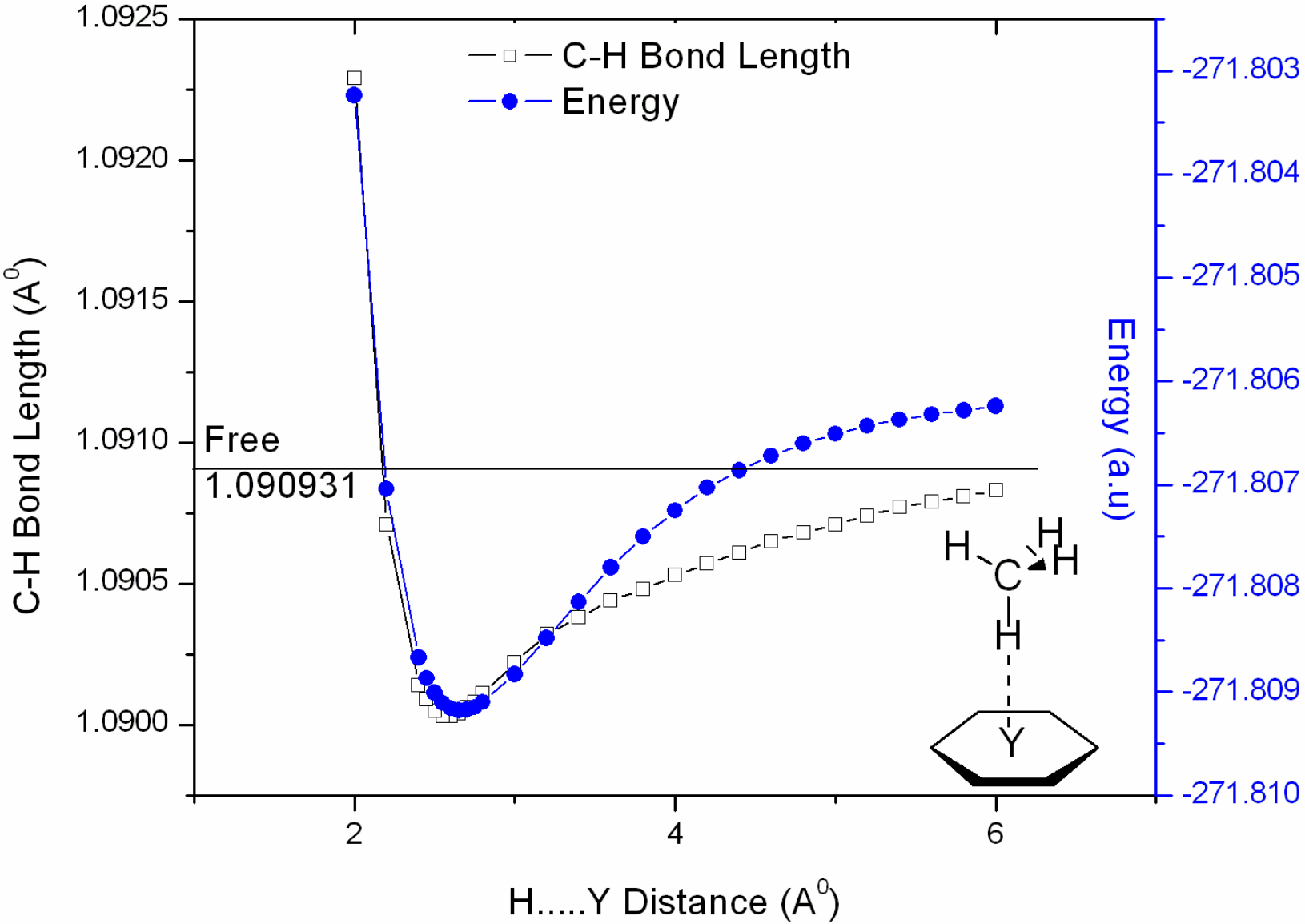
In many examples, near the equilibrium distance X-H bond Lengthens from a "pre-shortened" form.

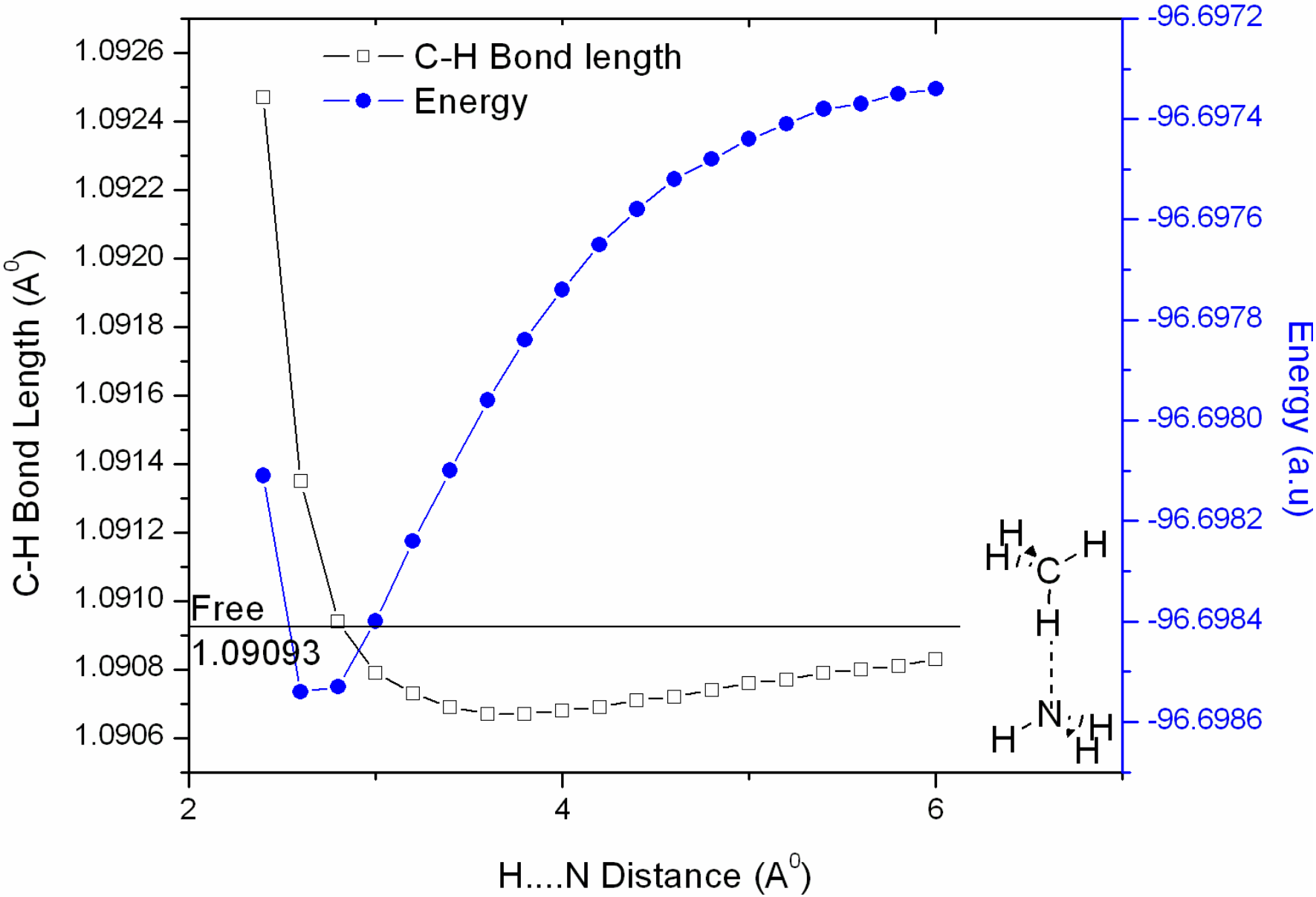
Three Examples

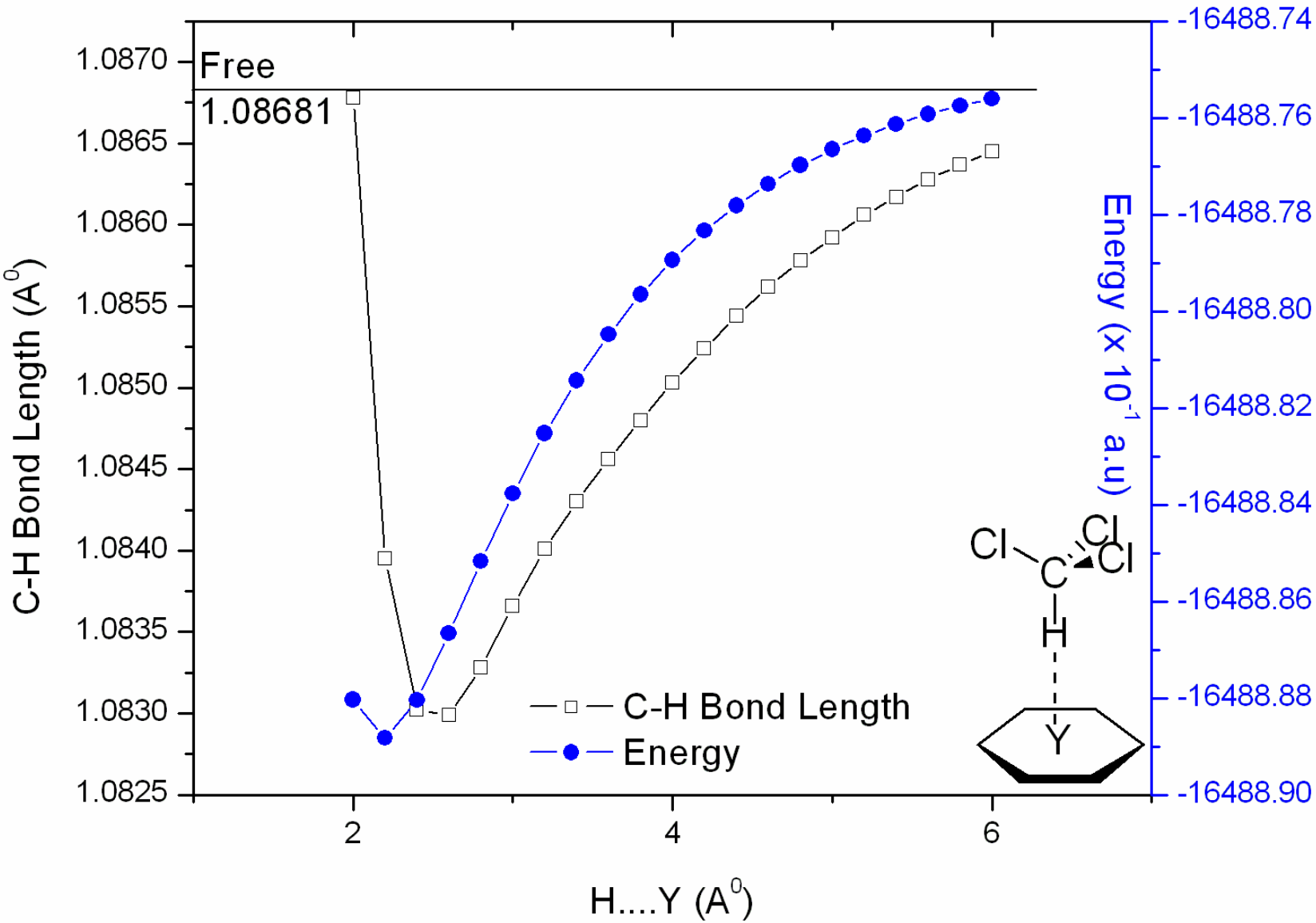
C_6H_5-------HCH3 BLUE SHIFT

CH4-------NH3 RED SHIFT

C6H6------HCCl3 BLUE SHIFT


C-H Bond Length
Energy
Free
1.090931
C-H Bond Length (A0)
Energy (a.u)
H.....Y Distance (A0)
1.0925
1.0920
1.0915
1.0910
1.0905
1.0900
-271.803
-271.804
-271.805
-271.806
-271.807
-271.808
-271.809
-271.810
2
4
6
H
H
H
C
H
Y


C-H Bond length
Energy
Free
1.09093
C-H Bond Length (A0)
Energy (a.u)
H....N Distance (A0)
1.0926
1.0924
1.0922
1.0920
1.0918
1.0916
1.0914
1.0912
1.0910
1.0908
1.0906
-96.6972
-96.6974
-96.6976
-96.6978
-96.6980
-96.6982
-96.6984
-96.6986
2
4
6
H
H
C
H
H
N
H
H
H


Free
1.08681
C-H Bond Length
Energy
C-H Bond Length (A0)
Energy (x 10-1 a.u)
H....Y (A0)
1.0870
1.0865
1.0860
1.0855
1.0850
1.0845
1.0840
1.0835
1.0830
1.0825
-16488.74
-16488.76
-16488.78
-16488.80
-16488.82
-16488.84
-16488.86
-16488.88
-16488.90
2
4
6
Cl
Cl
Cl
C
H
Y

Redistribution of Electron Density

Considerable amount of charge transfer from H bond acceptor is 'directed' to remote part of H bond donor . Very less charge transfer to sigma* X-H bond. The charge gain at the remote part triggers an internal rearrangement of H bond donor and its effect is X-H bond shortening.

Why the NBO charge transfer is different for different HB donors? How a rearrangement causes X-H bond contraction? Both Blue-shifting and Redshifting HB's have similar electron density Shifts in several examples.

Electric Field causes the shortening

An X-H bond having a negative dipole derivative shortens under a weak negative electric field. X-H bond shortening is, therefore, due to the weak HB acceptor. Enhanced shortening at equilibrium than 'point charge model prediction' occurs due to Pauly repulsion.

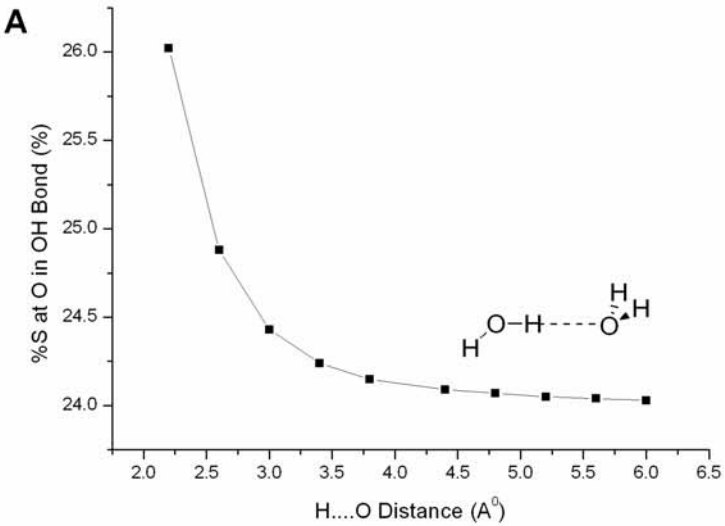
Why different X-H bonds have different dipole derivatives?

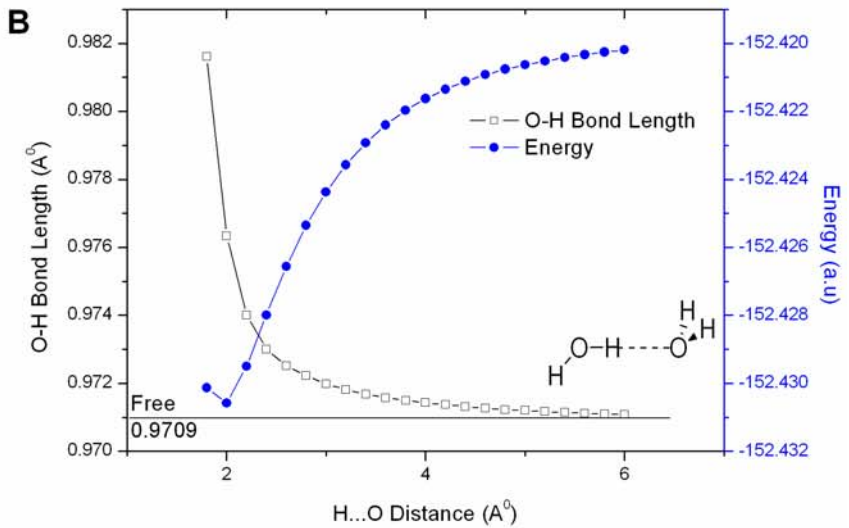
Why charge transfer causes enhanced X-H bond contraction?

Hybridization

% s character at X of the X-H bond increases continuously when a proton acceptor approaches the proton donor. For improper H bond, the lengthening effect of (negative) hyper conjugation is unable to overcome the shortening caused by this hybridization change.

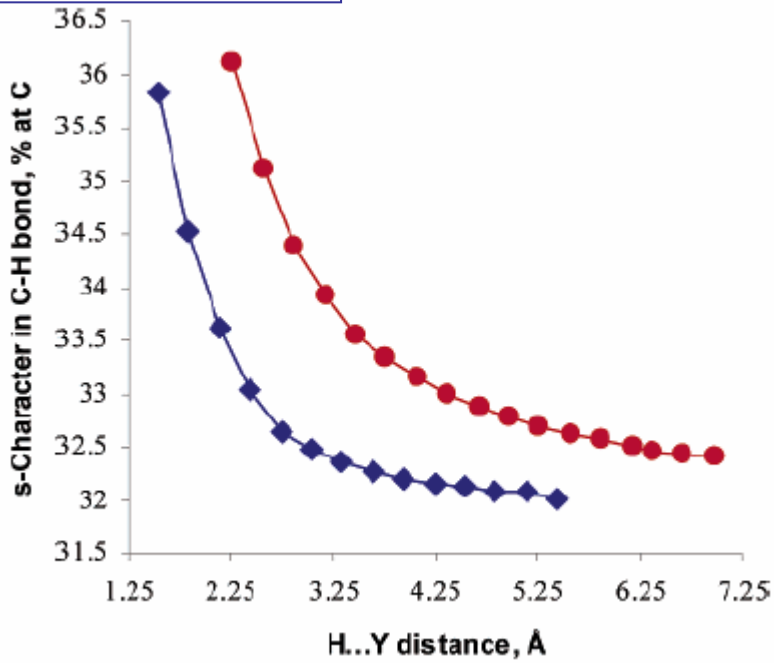
%s character increases in case of proper H bond donors too, but some never shows improper behavior.

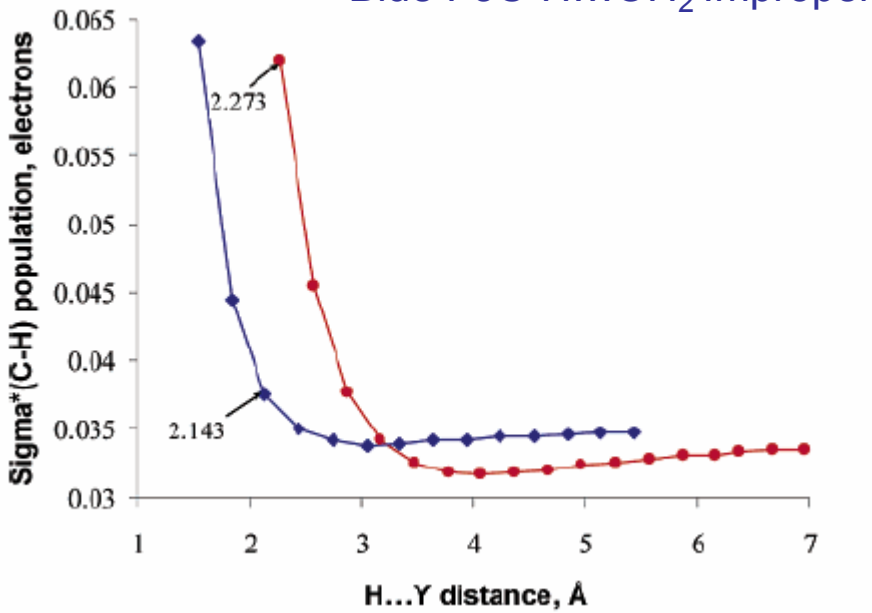

A
%S at O in OH Bond (%)
26.0
25.5
25.0
24.5
24.0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
H....O Distance (A0)
O–H
H
O
H
H

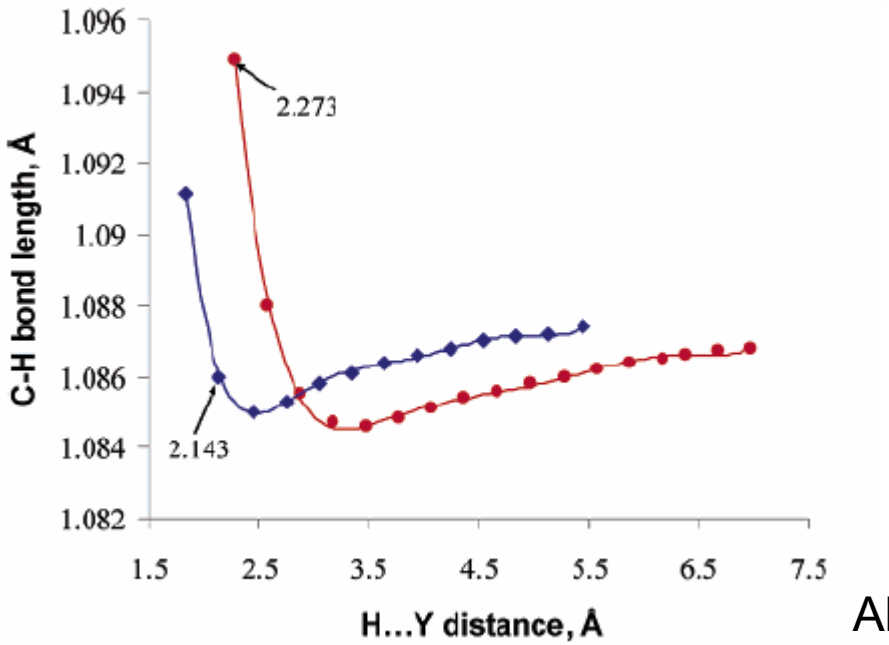

B
O-H Bond Length (A0)
0.982
0.980
0.978
0.976
0.974
0.972
0.970
-152.420
-152.422
-152.424
-152.426
-152.428
-152.430
-152.432
Energy (a.u)
O-H Bond Length
Energy
Free
0.9709
2
4
6
H...O Distance (A0)
O–H
H
O
H
H

4. Rehybridization

Red F3C-H…Cl Proper
Blue F3C-H…OH_2 Improper

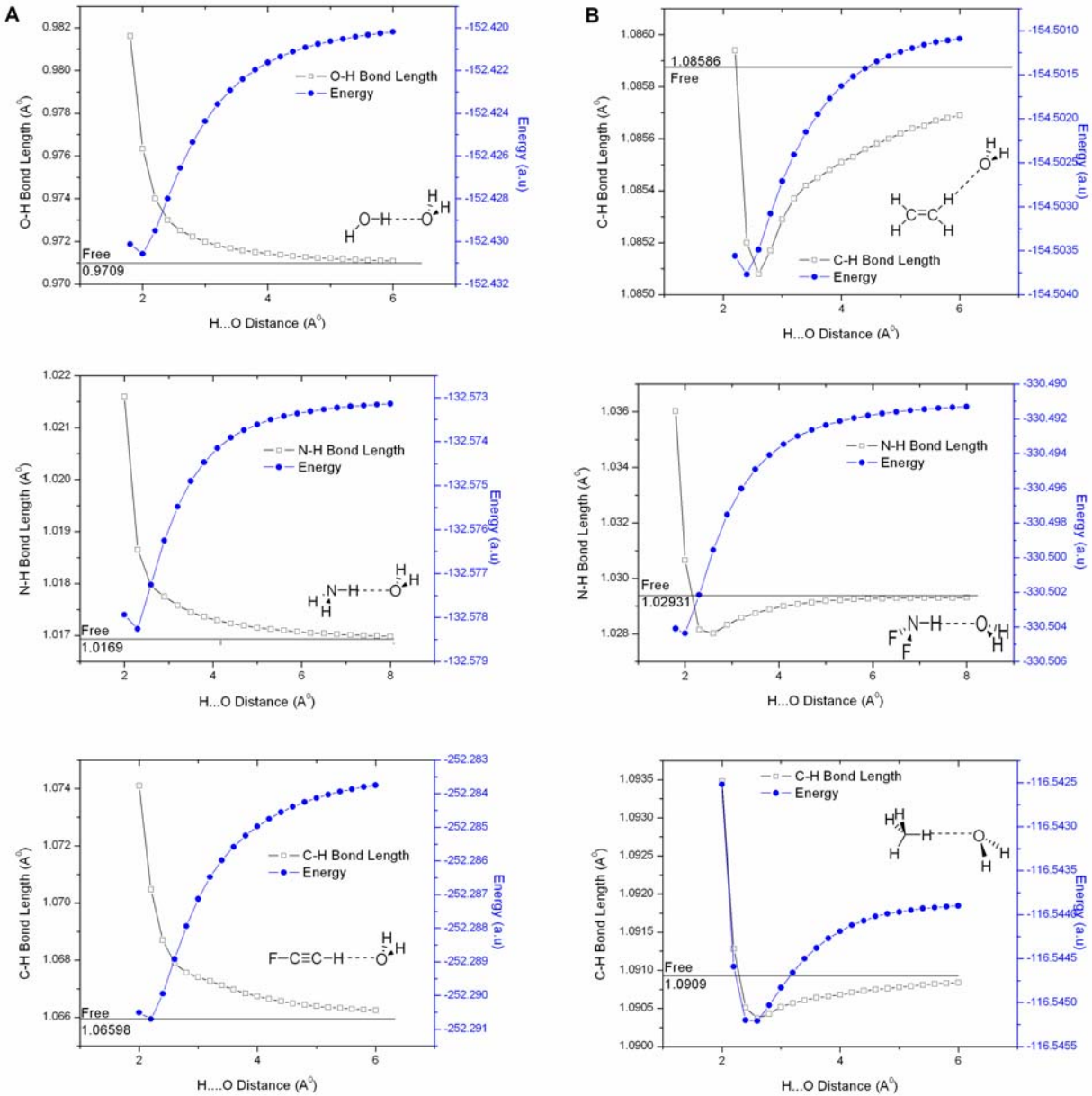


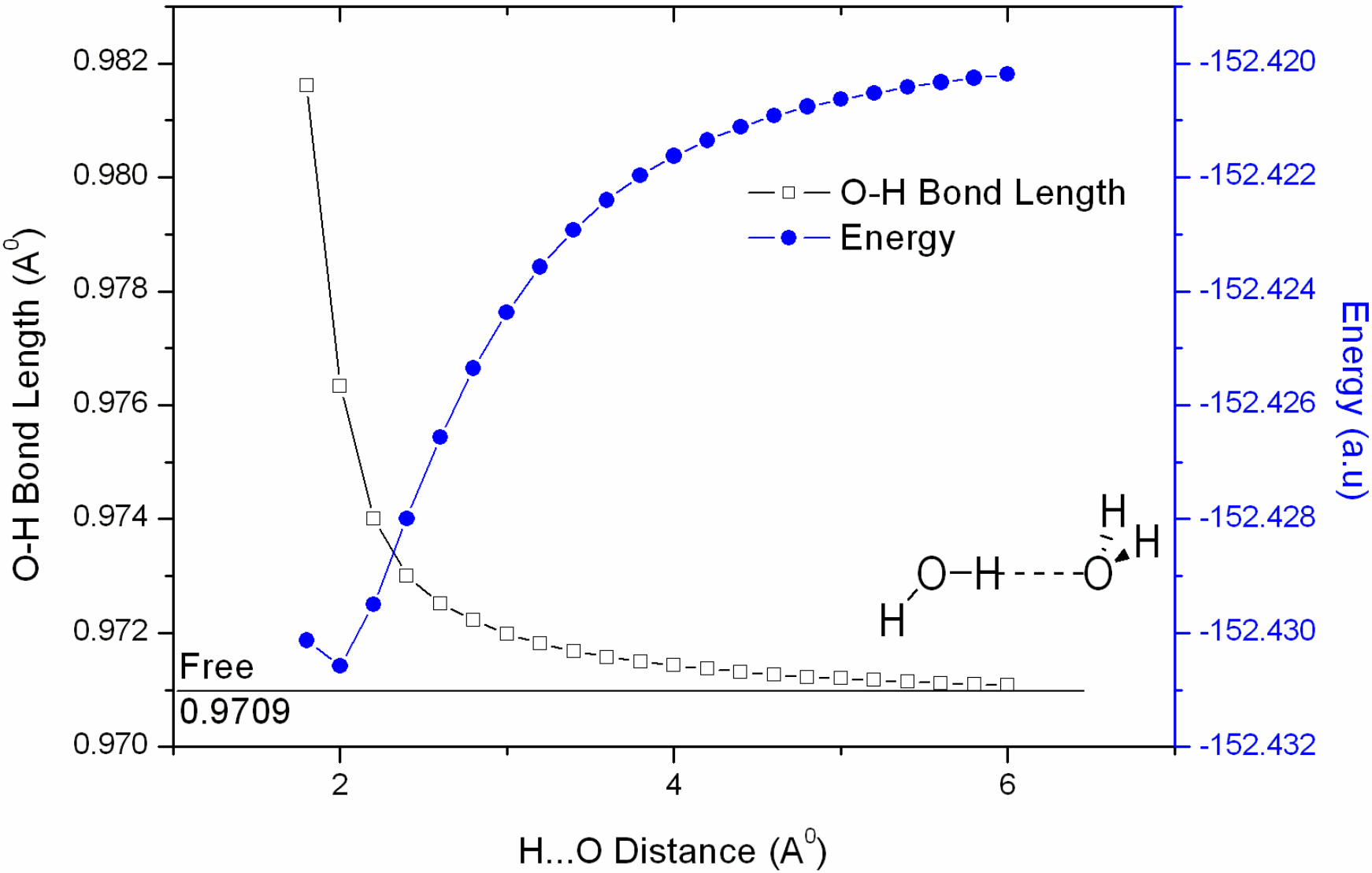


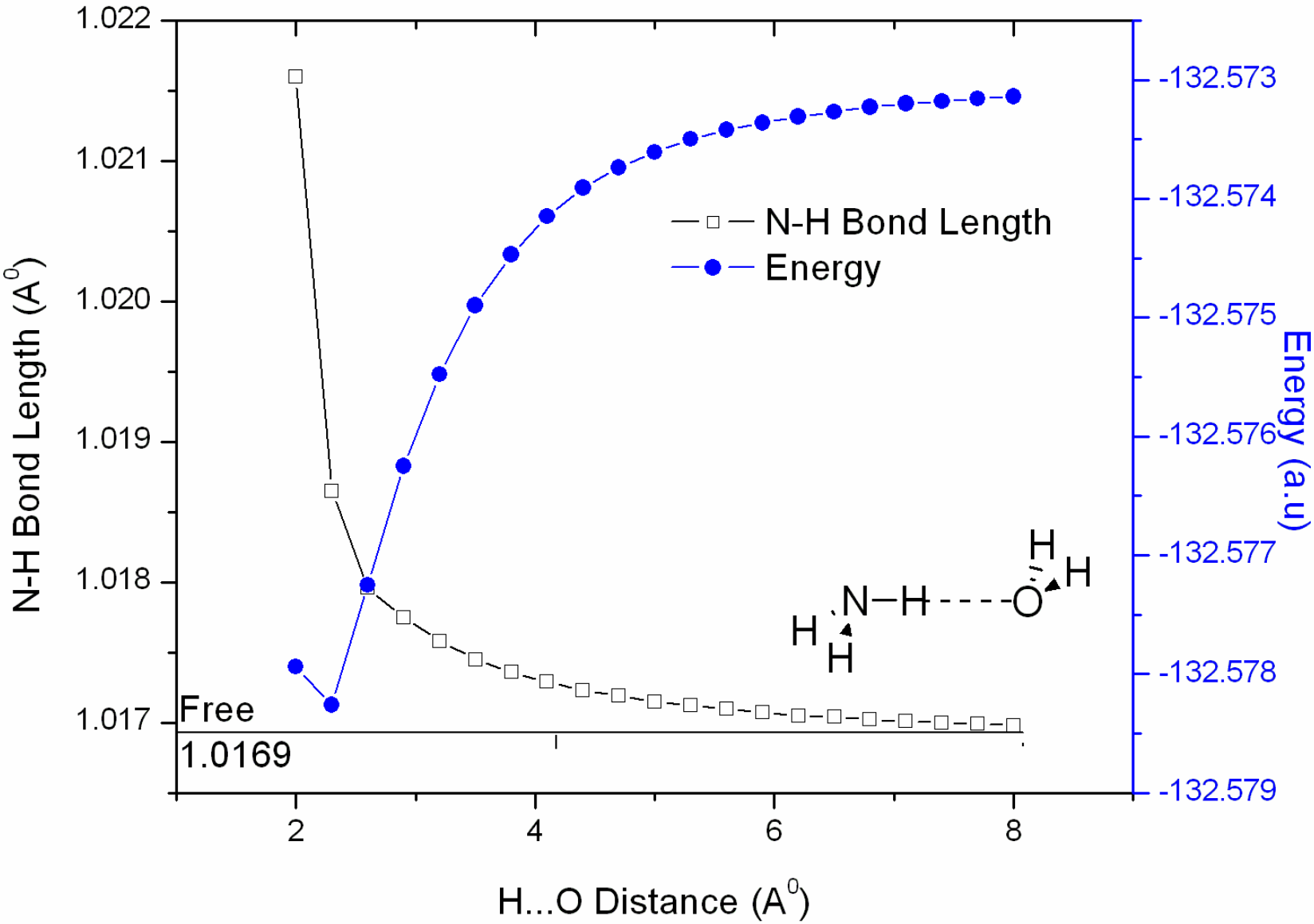


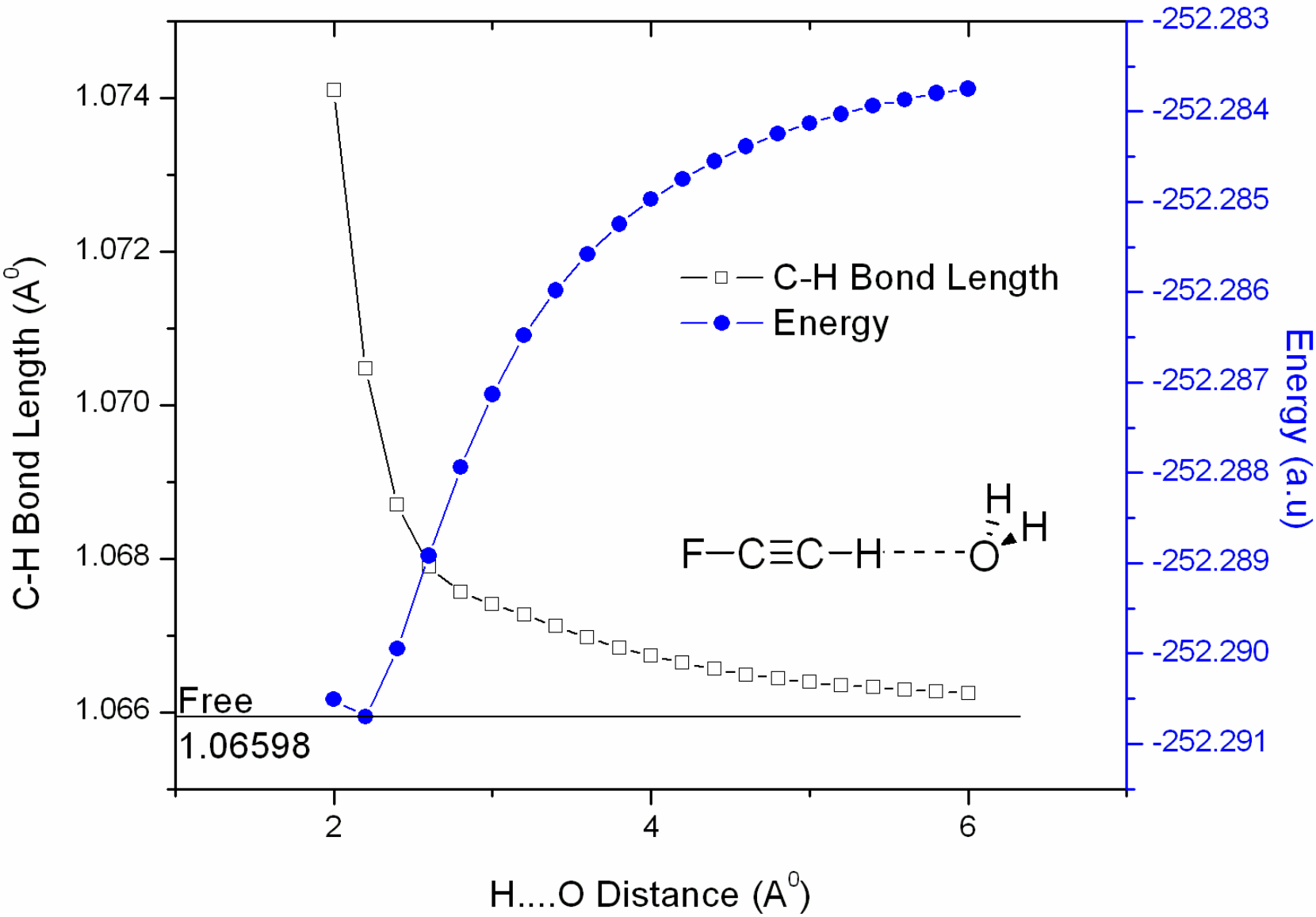
Alabugin, I. V et. al. *JACS.* ***2003****, 125, 5973.*

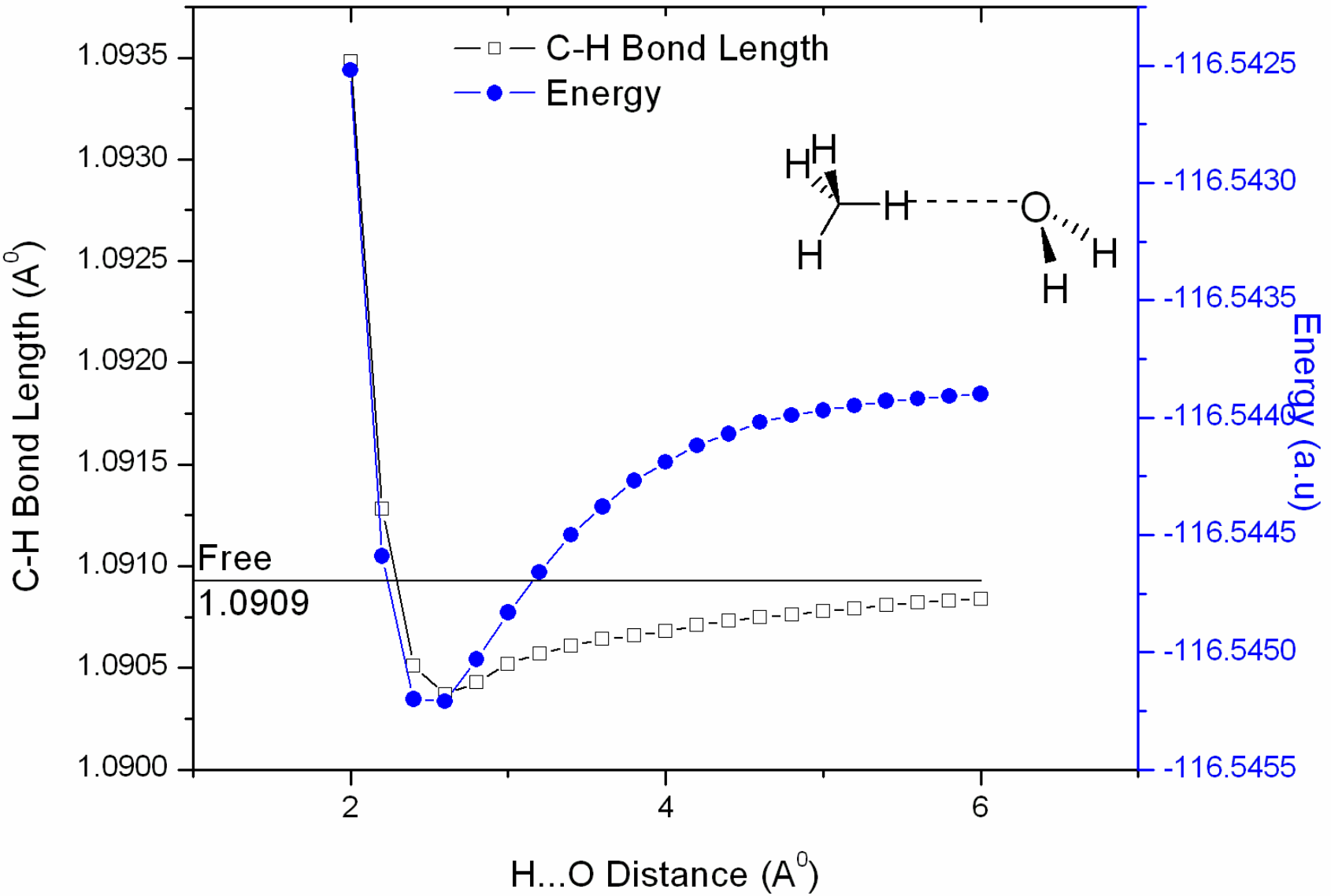
A Unified Explanation

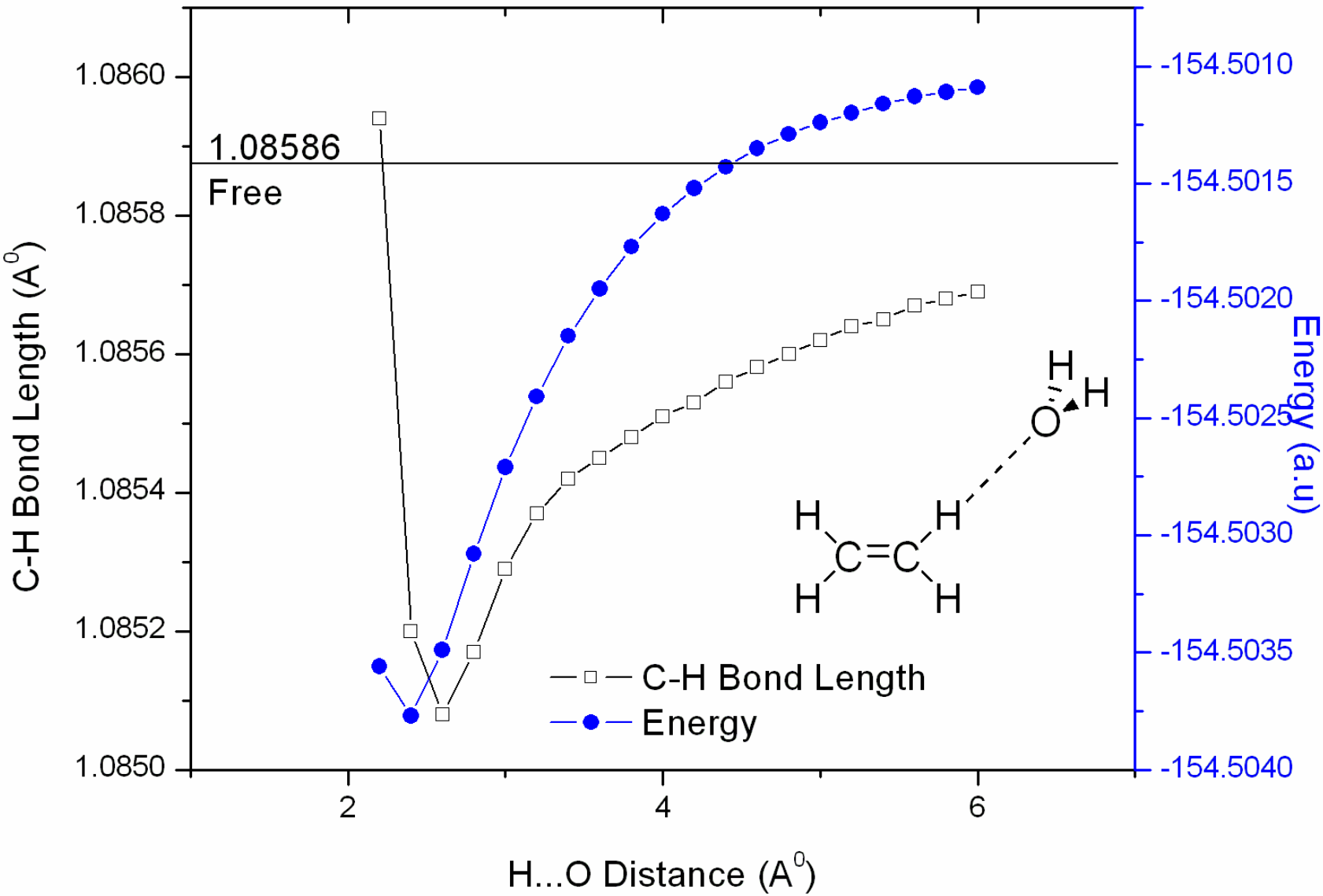


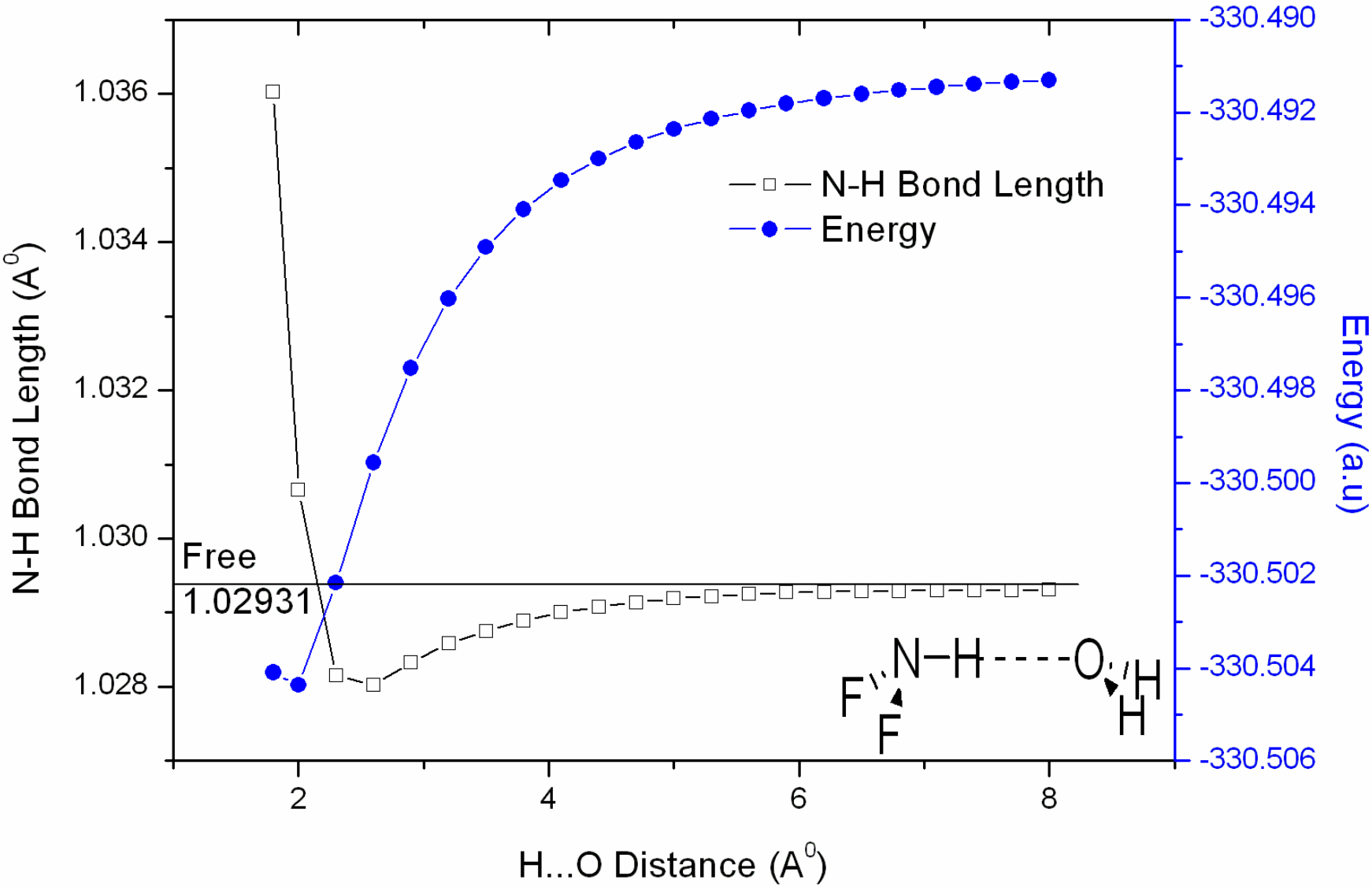

0.982
0.980
0.978
0.976
0.974
0.972
0.970
O-H Bond Length (A0)
-152.420
-152.422
-152.424
-152.426
-152.428
-152.430
-152.432
Energy (a.u)
2
4
6
H...O Distance (A0)
O-H Bond Length
Energy
Free
0.9709
H
O
H
H
O
H


1.022
1.021
1.020
1.019
1.018
1.017
N-H Bond Length (A0)
-132.573
-132.574
-132.575
-132.576
-132.577
-132.578
-132.579
Energy (a.u)
N-H Bond Length
Energy
Free
1.0169
2
4
6
8
H...O Distance (A0)
H
N
H
H
H
O
H


C-H Bond Length (A0)
1.074
1.072
1.070
1.068
1.066
Free
1.06598
2
4
6
H....O Distance (A0)
-252.283
-252.284
-252.285
-252.286
-252.287
-252.288
-252.289
-252.290
-252.291
Energy (a.u)
C-H Bond Length
Energy
F—C≡C—H----O
H
H


C-H Bond Length
Energy
C-H Bond Length (A0)
Energy (a.u)
H...O Distance (A0)
Free
1.0909
1.0935
1.0930
1.0925
1.0920
1.0915
1.0910
1.0905
1.0900
-116.5425
-116.5430
-116.5435
-116.5440
-116.5445
-116.5450
-116.5455
2
4
6
H
H
H
H
O
H


1.0860
1.0858
1.0856
1.0854
1.0852
1.0850
C-H Bond Length (A0)
1.08586
Free
-154.5010
-154.5015
-154.5020
-154.5025
-154.5030
-154.5035
-154.5040
Energy (a.u)
2
4
6
H...O Distance (A0)
H
H
O
H
C=C
H
H
C-H Bond Length
Energy


N-H Bond Length
Energy
Free
1.02931
N–H - - - O
F
F
H
H
N-H Bond Length (A0)
Energy (a.u)
H...O Distance (A0)
1.036
1.034
1.032
1.030
1.028
-330.490
-330.492
-330.494
-330.496
-330.498
-330.500
-330.502
-330.504
-330.506
2
4
6
8

Based on Equilibrium Geometry	
Proper (Red shift, Bond lengthening)	**Improper (Blue shift, Bond Shortening)**
H_2O, HF, NH_3, HCl, etc with all HB acceptors.[4]	CHF_3 with FH, ClH, OH_2, SH_2 and with pi donors such as benzene, acetylene etc.[1a,9,14]
HCCH, HCN with H2O, [7d] Pi acceptors[1b]	CHF_2Cl, $CHFCl_2$ with oxygen donors.[1j]
CHF_3 with electron donor like Cl^-, F^-, $N(CH_3)_3$, $NH(CH_3)_2$. [9,14]	CH_4 with pi donors[1g] with H_2O, MeOH, H_2CO.[7a]
CH_4 with Cl^-.[1i]	Benzene dimer.[1b]
	X-Ig-H with OC, N_2, CO, H_2O etc.[25,26]
	F_3SiH with various HB acceptors.[9,27]
	F_2NH with FH[9, 28] F_4PH dimer. [29]

Based on HB Donor	
Proper (Red shift, Bond lengthening)	**Pro-improper (Blue/Red Shift, Bond shortening/lengthening)**
H_2O, FOH, HF, NH_3, HCl, HF etc $F_2C{=}CH_2$ HCCH, HCN, FCCH,	Alkanes, Alkenes, Aldehydes, CH_xF_{4-x}, CH_xCl_{4-x}, C_6H_6 F_3SiH, F_2NH, F_2PH, F_4PH X-Ng-H, (X = F, Cl, OH; Ng = noble gas)

A

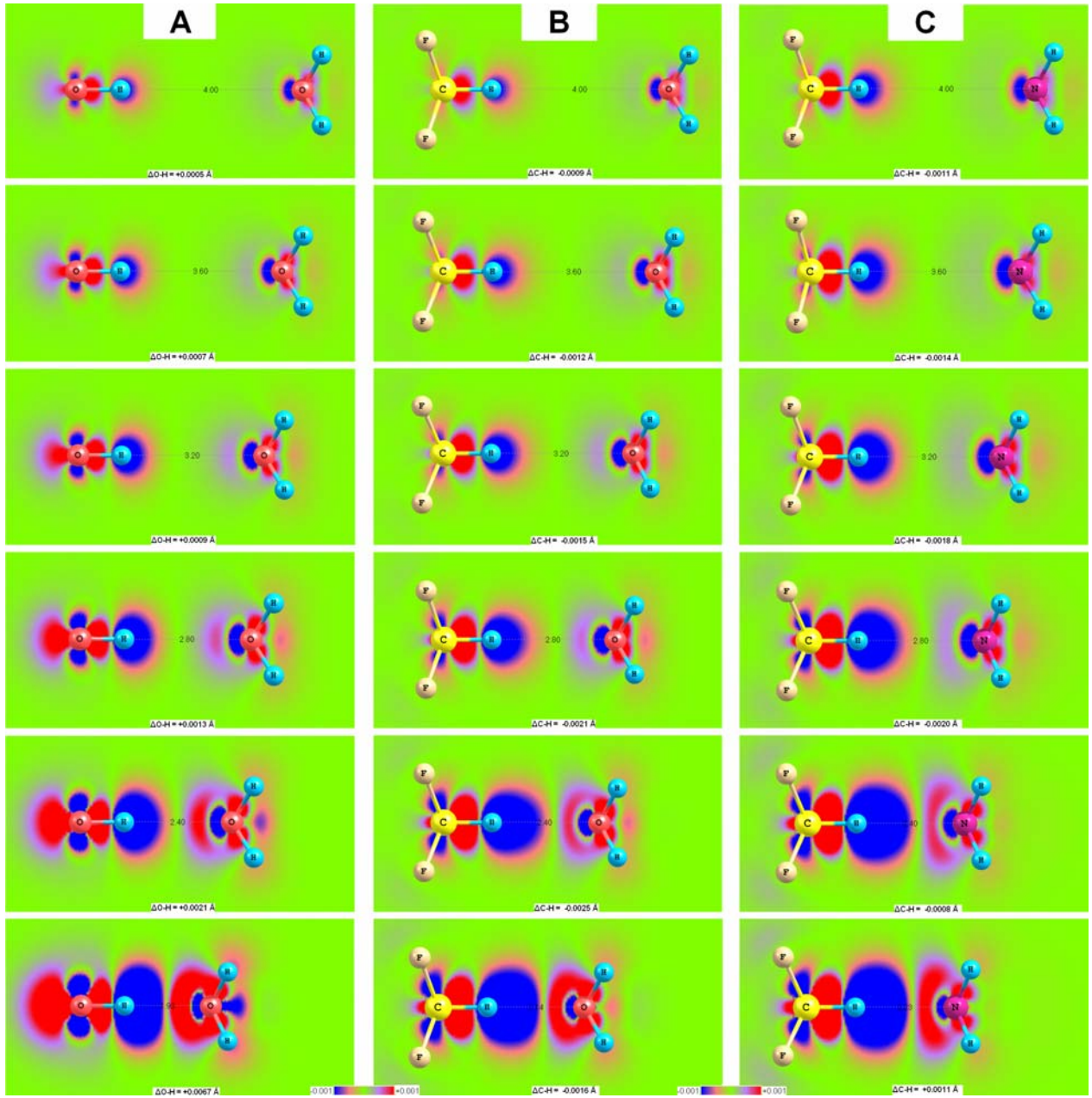
HO-H…OH2

B

F3C-H…OH2

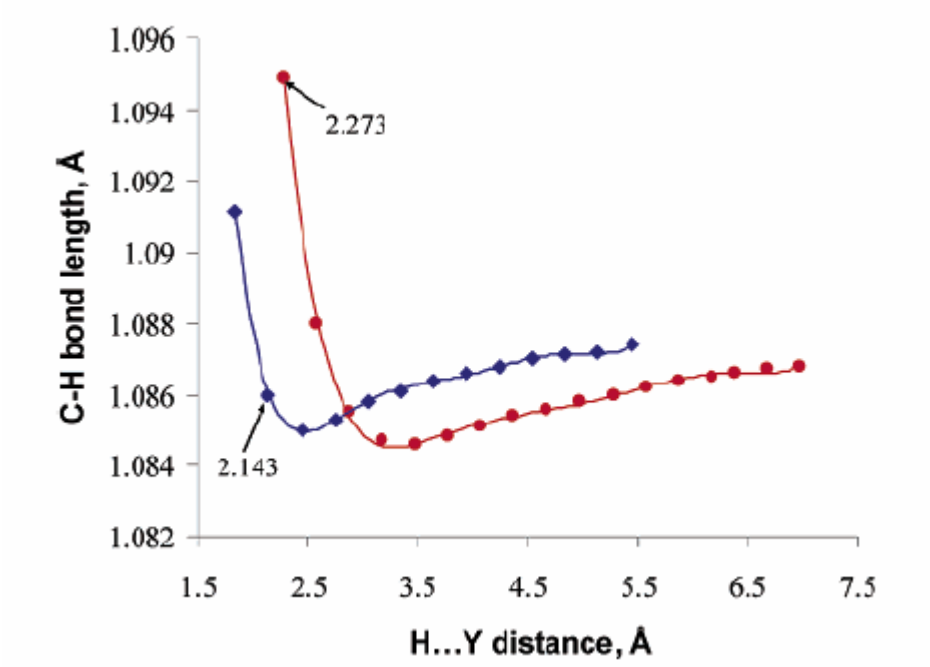
C

F3C-H…NH3



F3CH---Cl-

F3CH---OH2



H3C-H	1.0909
F3C-H	1.0876
CH3-CC-H	1.0678
HCC-H	1.0677
FCC-H	1.0660
H2CCH-H	1.0859
FHCCH-H	1.0834
F2CCH-H	1.0803
F2CCF-H	1.0801

HO-H	0.9709
FO-H	0.9813
H2N-H	1.0169
F2N-H	1.0293

Origin of Electron Density Shift

1. X. H.
2. X H

   δ- —— δ+

3. X——H…….Y

   δ-- δ++ δ-

4. X-H bond contraction in presence of Y.

A. Electronegativity of X.

B. The more electro negative the X, the more electron deficient the RHS of H, the more charged the atoms, the more electron rich the bond and the more short the bond.

C. Electron withdrawing of X, and depletion at RHS of H leads to the distribution as found at free monomer, to make the molecule stable.

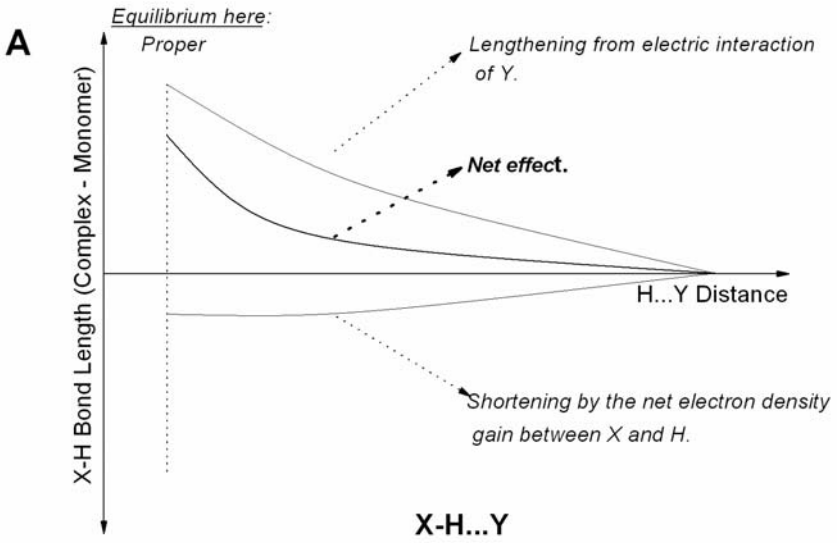
D. The remaining 'e.d. at RHS' of H in the free structure is needed to stabilize the molecule.

E. This stabilization can at least be maintained if the 'e.d. at RHS' is replaced by Y.

F. OR, electron withdrawing effect of X withdraw the 'e.d. at RHS' further in presence of Y.

G. B…….the more e.d. deficient the RHS of H, the more charged the atoms, the more electron rich the bond and the shorter the bond.

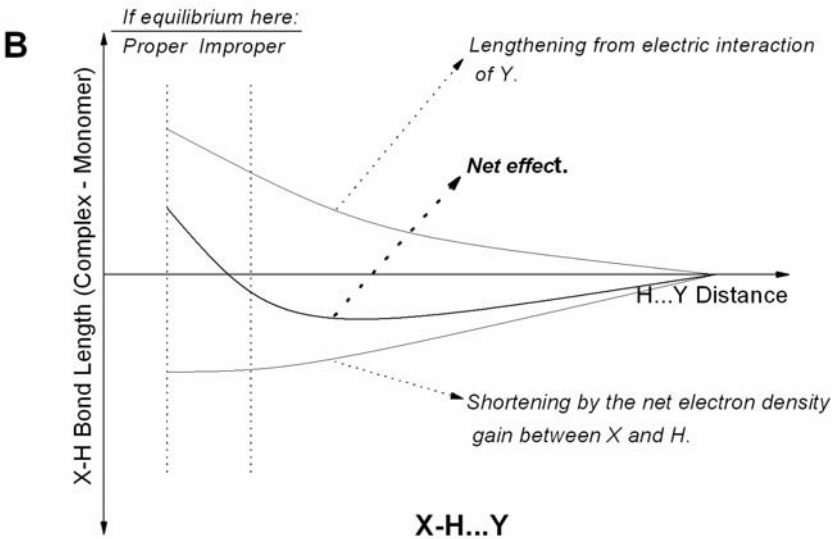
But, Many X-H Bonds are not Contracting….



A. **The more positive the H the stronger the lengthening effect due to Y.**

B. **The more positive the H, the less the e.d. available at H, for X to pull.**

C. **The more electron rich the bond, the less effect due to the e.d. shift.**



A. **The less positive the H the weaker the lengthening effect due to Y.**

B. **The less positive the H, the more the e.d. available at H, for X to pull.**

C. **The less electron rich the bond, the more effect due to the e.d. shift.**

Literature examples.

F-H…F-F_2C-H Karpfen, A.; Kryachko, E. S. *JPC-A, **2003**, 107, 9724.*

F-H…F-F_2Si-H Karpfen, A. *J. Mol.Str.(Theochem), **2004**, 710, 85.*

F-H…O=CH_2 Karpfen, A.; Kryachko, E. S. JPC-A, **2005**, 109, 8930.

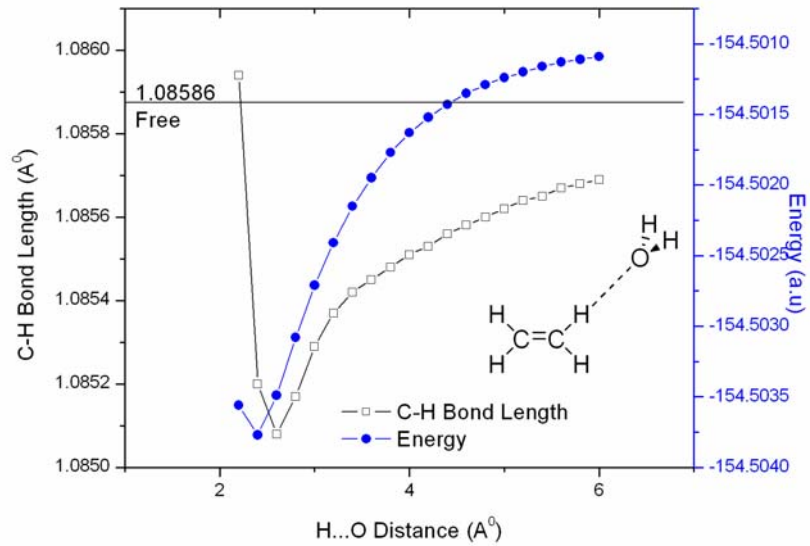
F-H…F-FN-H, F-H…F-FP-H, F-H…F-FAs-H Karpfen, A. *J. Mol.Str.(Theochem), **2005**, 757, 203.*

HO-H…O=S(CH_3)$_2$ Mrazkova, E.; Hobza, P. *JPC-A, **2003**, 107, 1032.*

HO-H…O(C4H9)(C2H4OH) Katsumoto, Y.; Komastu, H.; Ohno, K. *JACS, **2006**, 128,* 9278.

Converting pro-improper to proper

1



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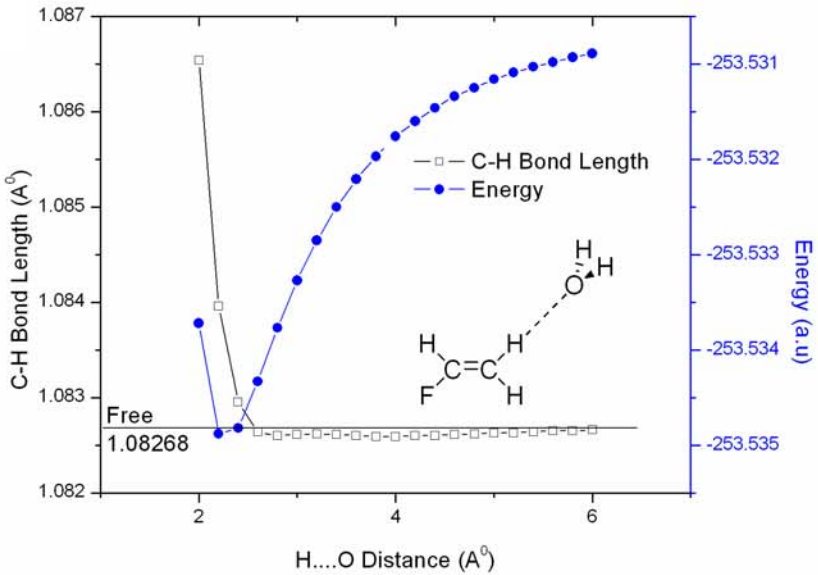

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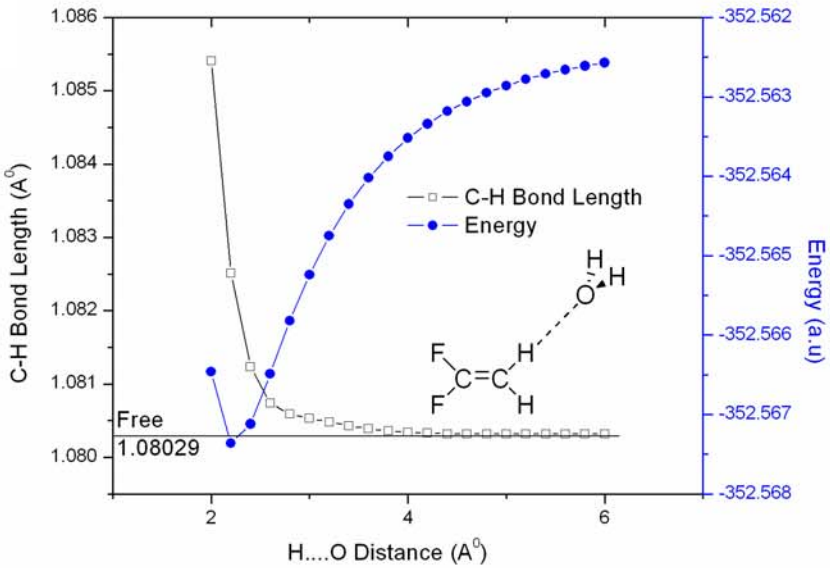

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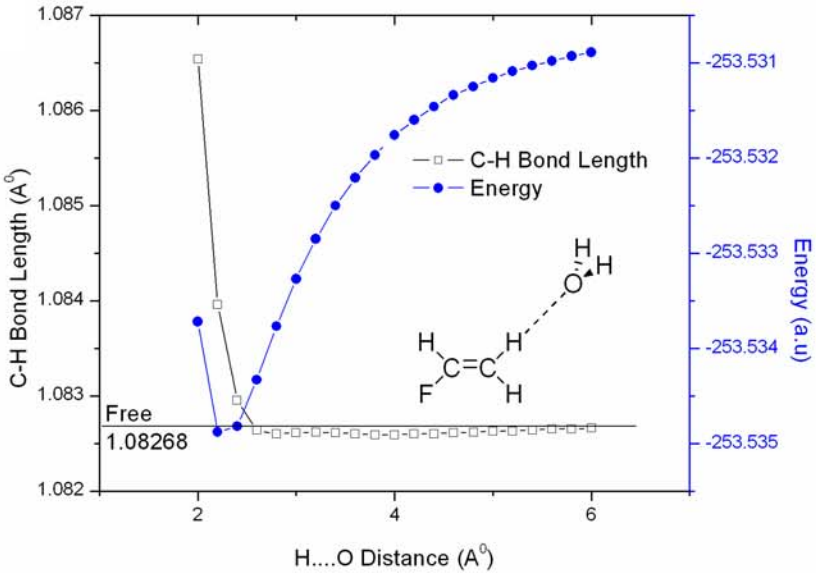
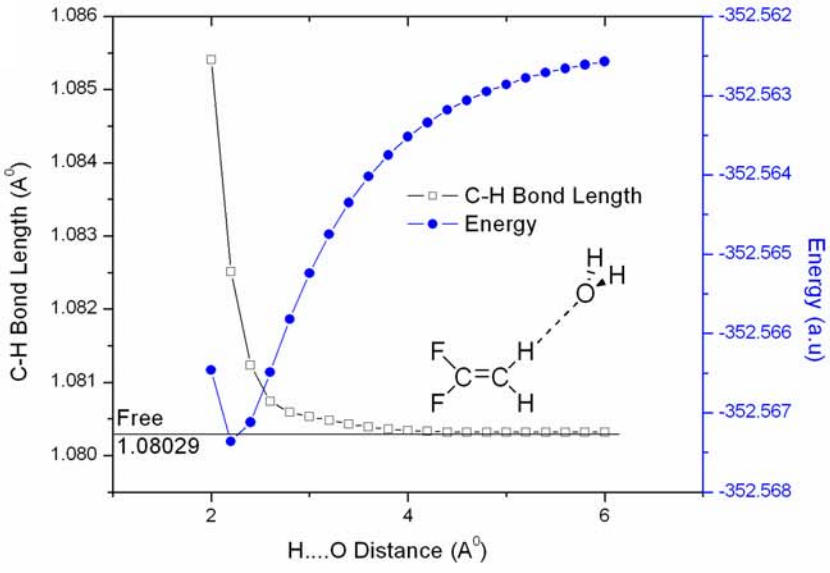

C-H Bond Length
Energy
Free
1.08268
C-H Bond Length (A⁰)
Energy (a.u)
H....O Distance (A⁰)
1.087
1.086
1.085
1.084
1.083
1.082
-253.531
-253.532
-253.533
-253.534
-253.535
2
4
6

3

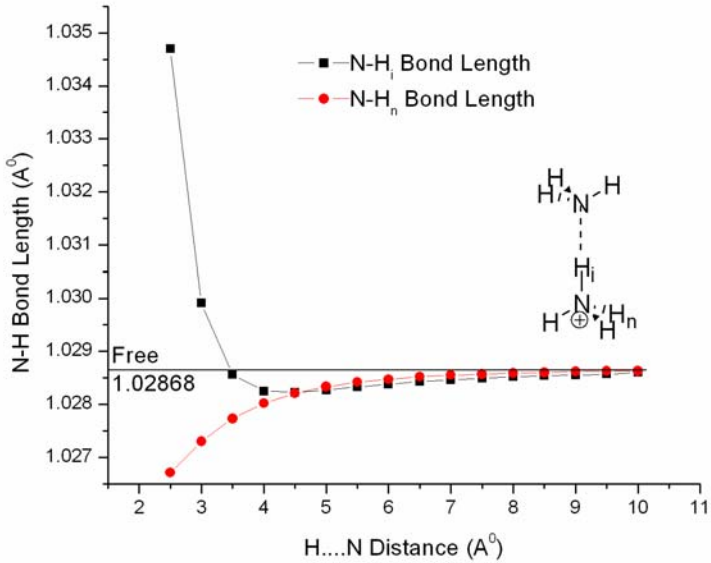

C-H Bond Length
Energy
Free
1.08029
C-H Bond Length (A⁰)
Energy (a.u)
H....O Distance (A⁰)
1.086
1.085
1.084
1.083
1.082
1.081
1.080
-352.562
-352.563
-352.564
-352.565
-352.566
-352.567
-352.568
2
4
6

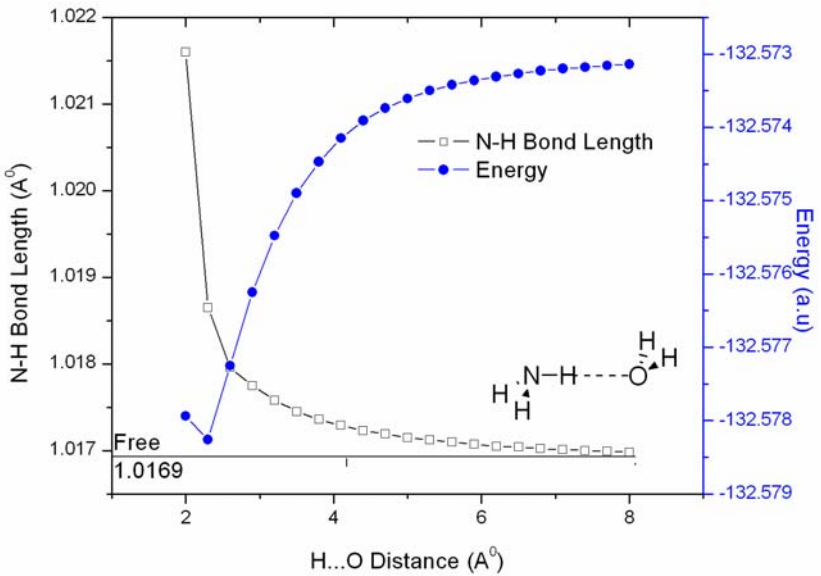
3. Converting proper to pro-improper

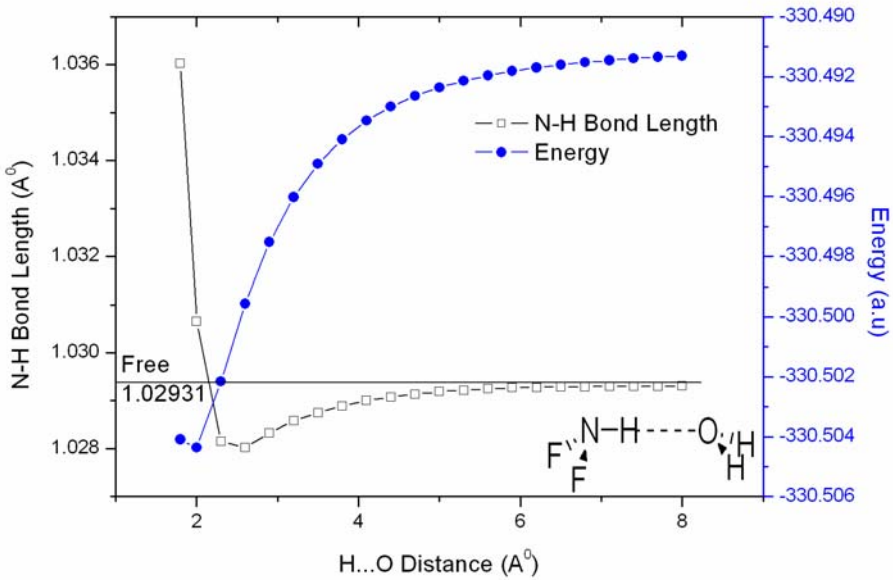
H_2N-H (1.0169 Å)

H_3N^+-H (1.0287 Å)

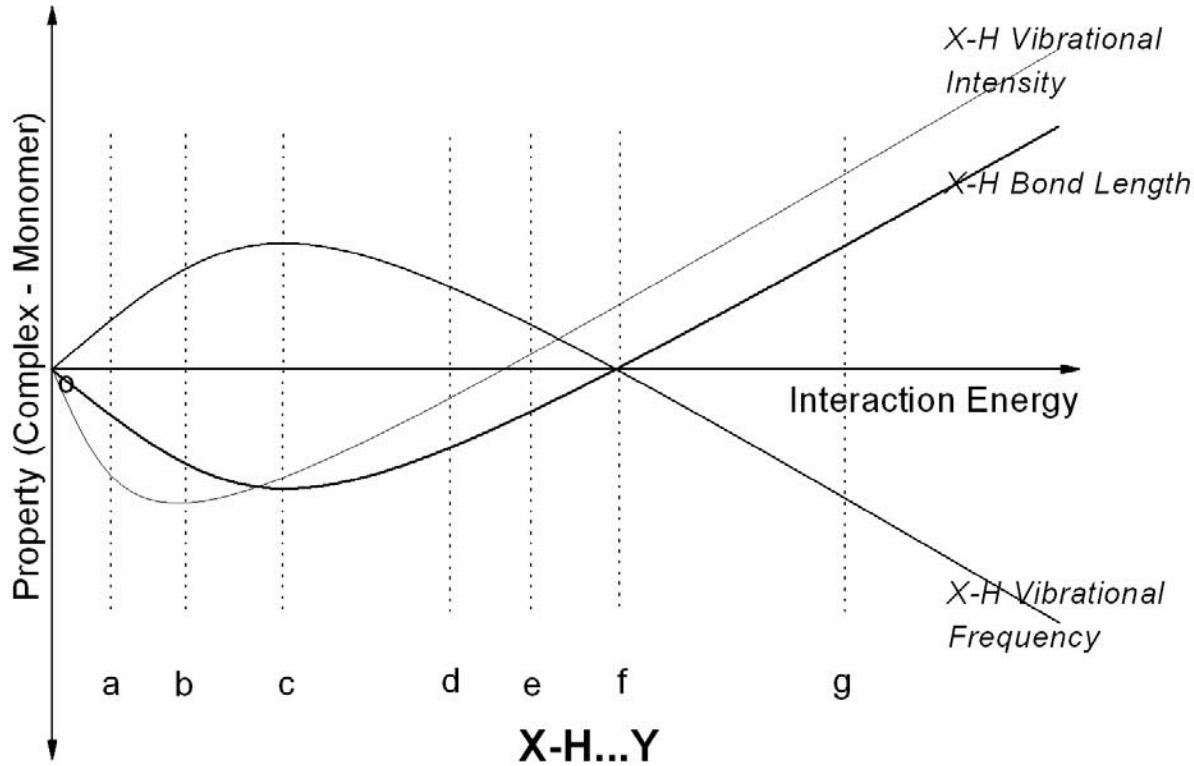
F_2N-H (1.0293 Å)





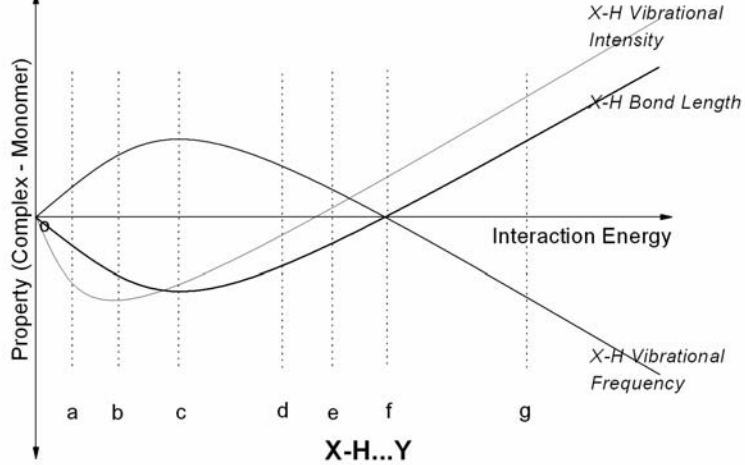


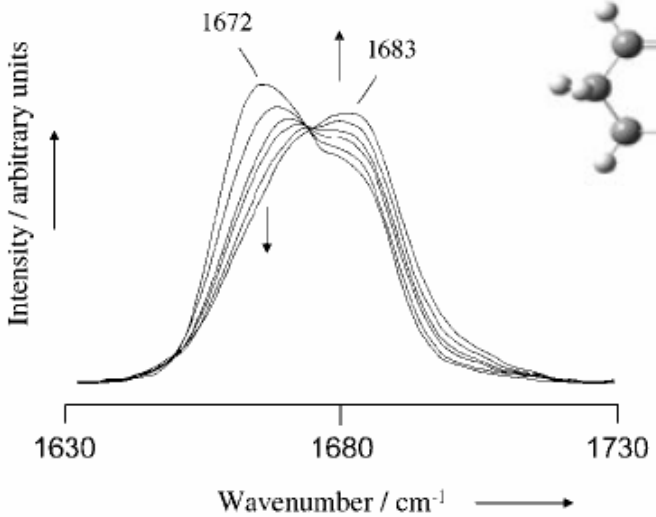
5. Effect of variation of Y.



6. HB with No Frequency Shift !

Region f





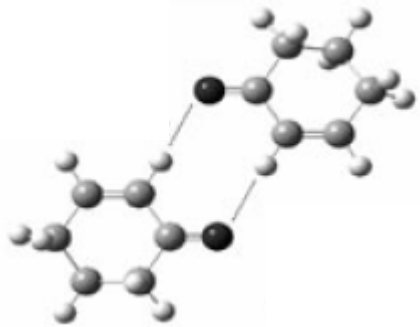


Figure 3. Raman spectra, normalized to unit area, of pure cyclohexenone at different temperatures in the νC=O region. The pseudo-isosbestic point is at about 1679 cm^{-1}. Increasing temperature promotes changes in the intensity of the bands that are denoted by the arrows.

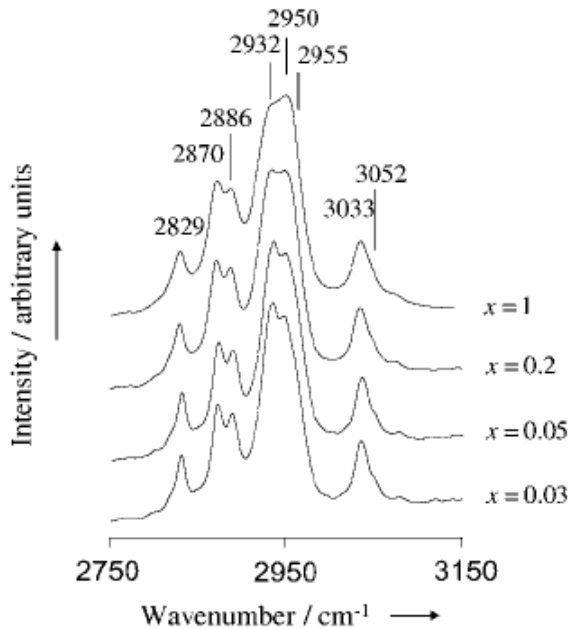
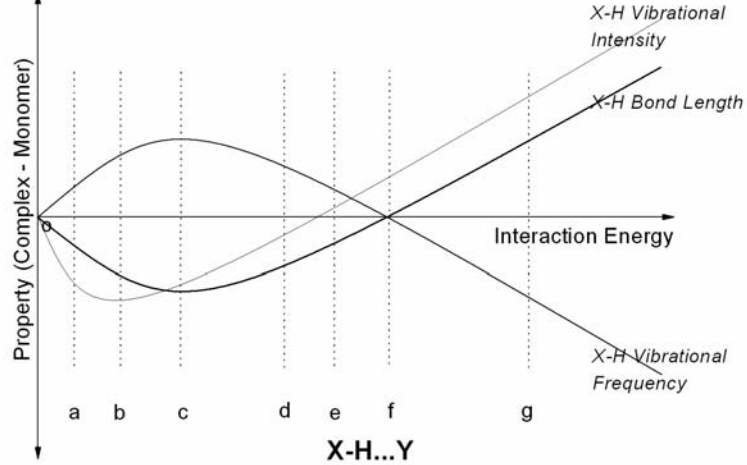


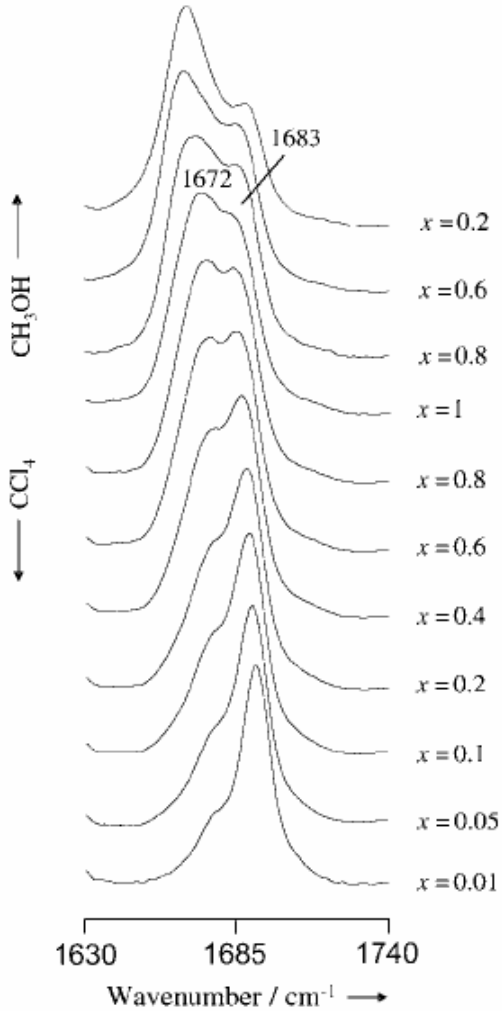
Figure 6. FTIR spectra of cyclohexenone in the region of the C–H stretching modes, for pure liquid and CCl_4 solutions.

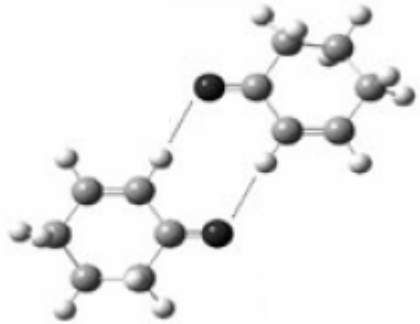
Nolasco, M. M.; Riberio-Claro, P. J. A. *Chem.Phys.Chem.* ***2005****, 6, 496*

6. HB with No Frequency Shift !

Region f







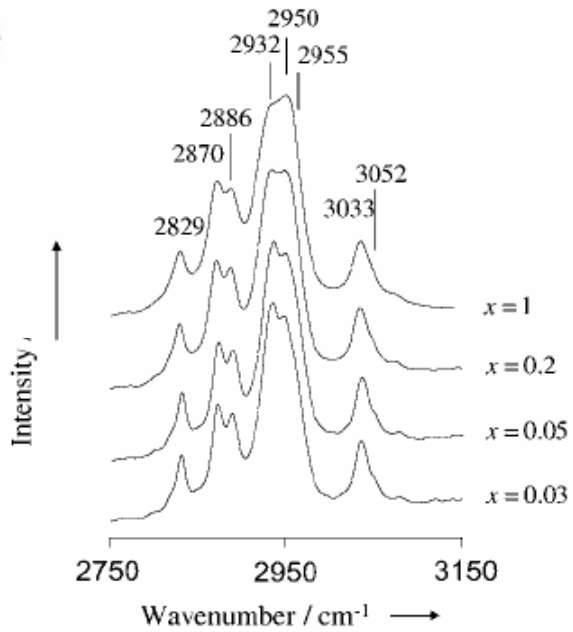


Figure 4. *Room-temperature Raman spectra of cyclohexenone solutions in CCl_4 and in CH_3OH, at different mole fractions (x), in the νC=O region.*

Figure 6. *FTIR spectra of cyclohexenone in the region of the C–H stretching modes, for pure liquid and CCl_4 solutions.*

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