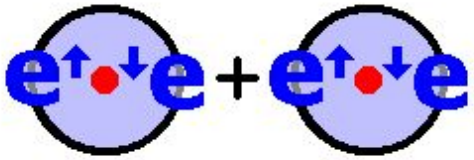
PROTEIN PHYSICS

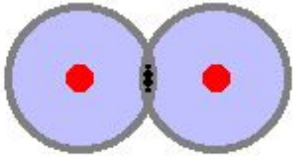
LECTURES 3-4

Elementary interactions:
Van der Waals
&
H-bonds



→ **do not bond;**

repulsion at small distances

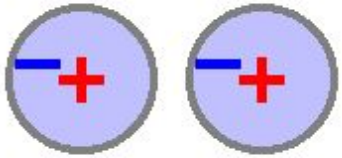
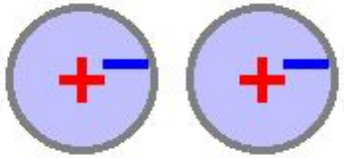
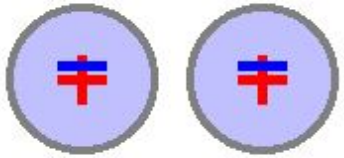


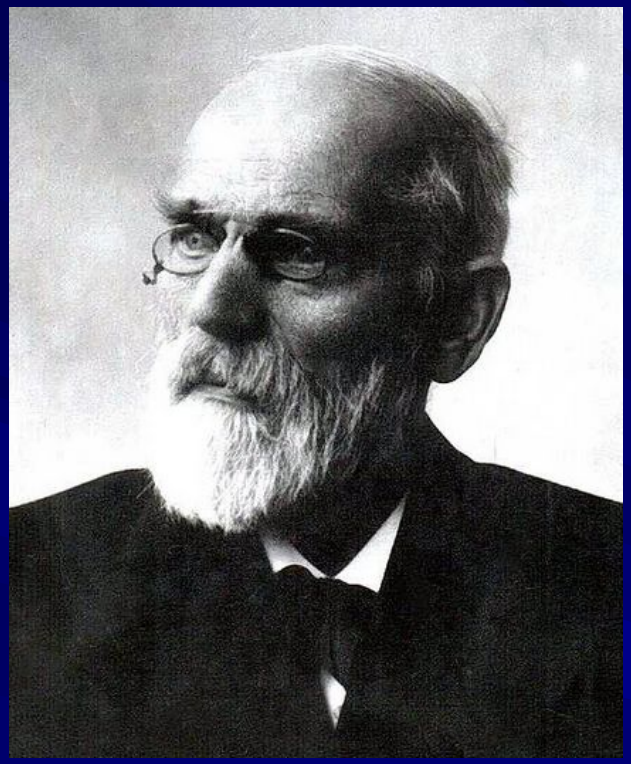
BUT:

Van der Waals

attraction at larger distances

due to coordination of e vibrations

better  or  than 



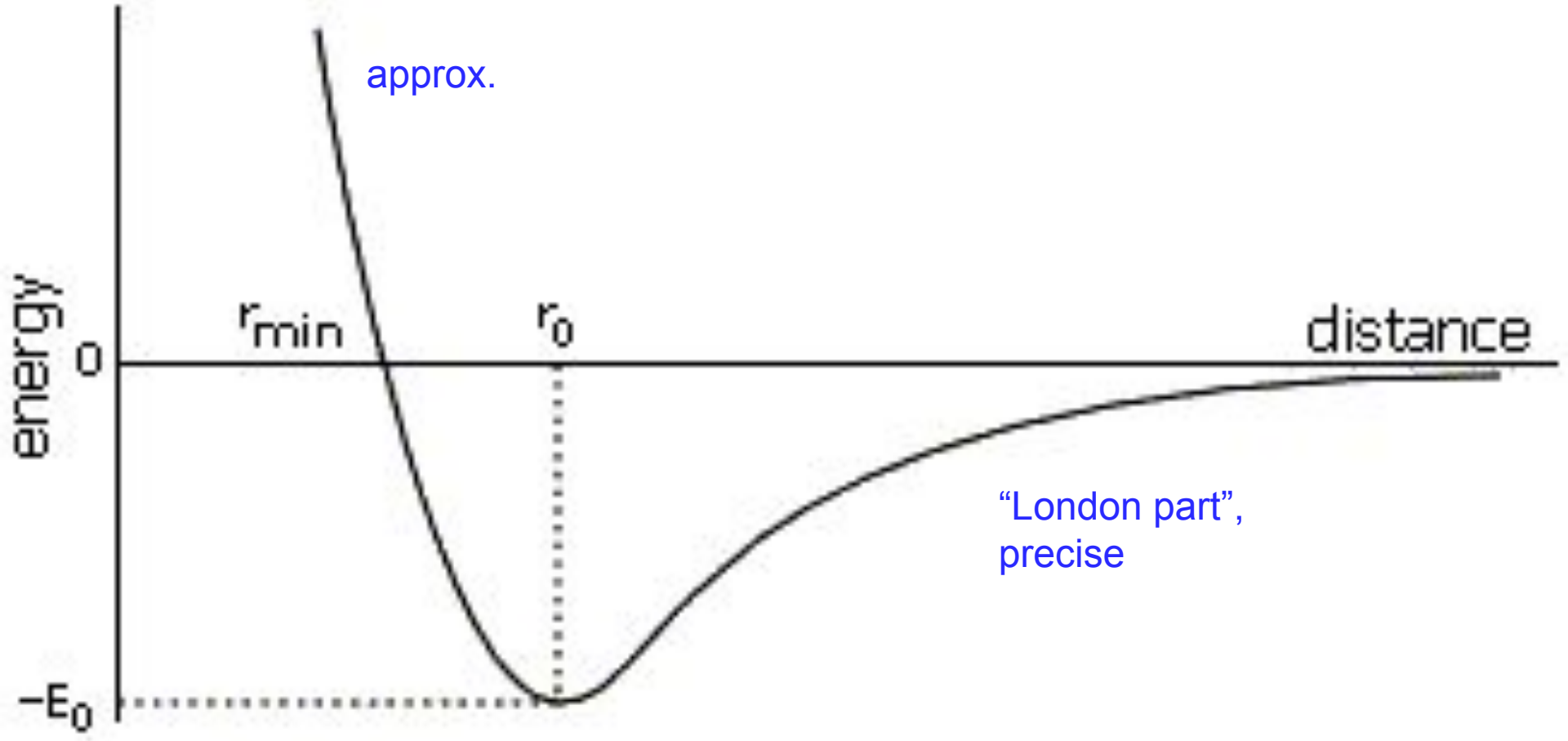
Johannes Diderik van der Waals
(1837 – 1923)
— Nobel Prize 1910

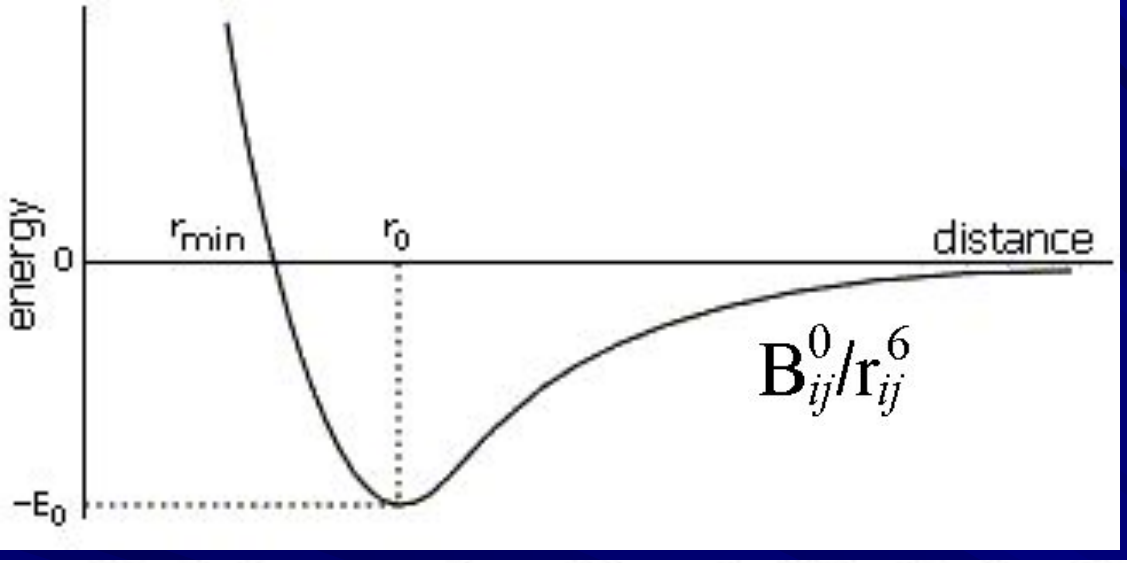
Fritz Wolfgang London
(1900 – 1954)

Lennard-Jones potential:

$$U_{LJ}(r) = E_0[(r_0/r)^{12} - 2(r_0/r)^6]$$

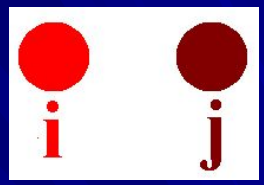
The simplest form





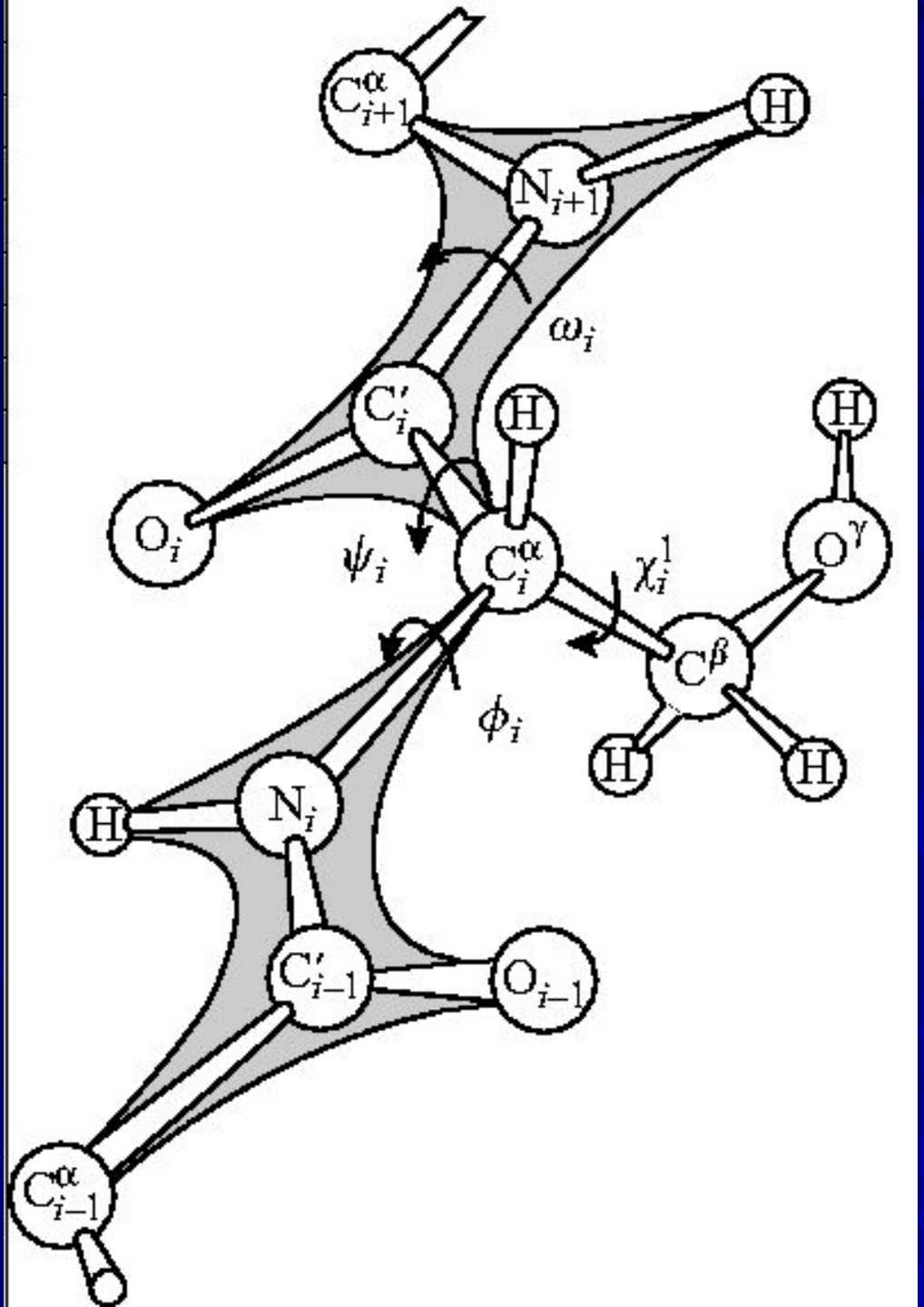
In vacuum

$$B^0_{ij} = \beta_i \beta_j$$



Typical parameters of van der Waals interaction potentials.

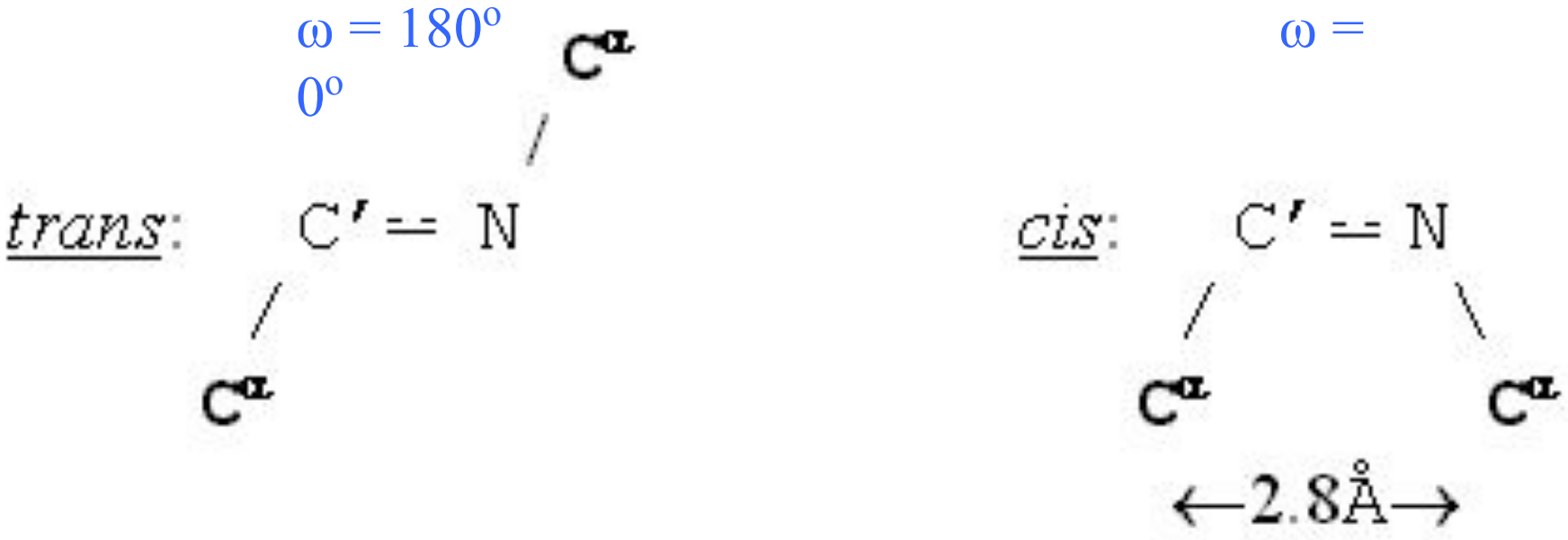
Interaction	E_0, $\frac{kcal}{mol}$	r_0, Å	r_{min}, Å	Min. v. d. Waals radii of atoms, Å	
H....H	0.12	2.4	2.0	H:	1.0
H....C	0.11	2.9	2.4		
C....C	0.12	3.4	3.0	C:	1.5
O....O	0.23	3.0	2.7	O:	1.35
N....N	0.20	3.1	2.7	N:	1.35
CH_2...CH_2	≈0.5	≈4.0	≈3.0	CH_2:	≈1.5



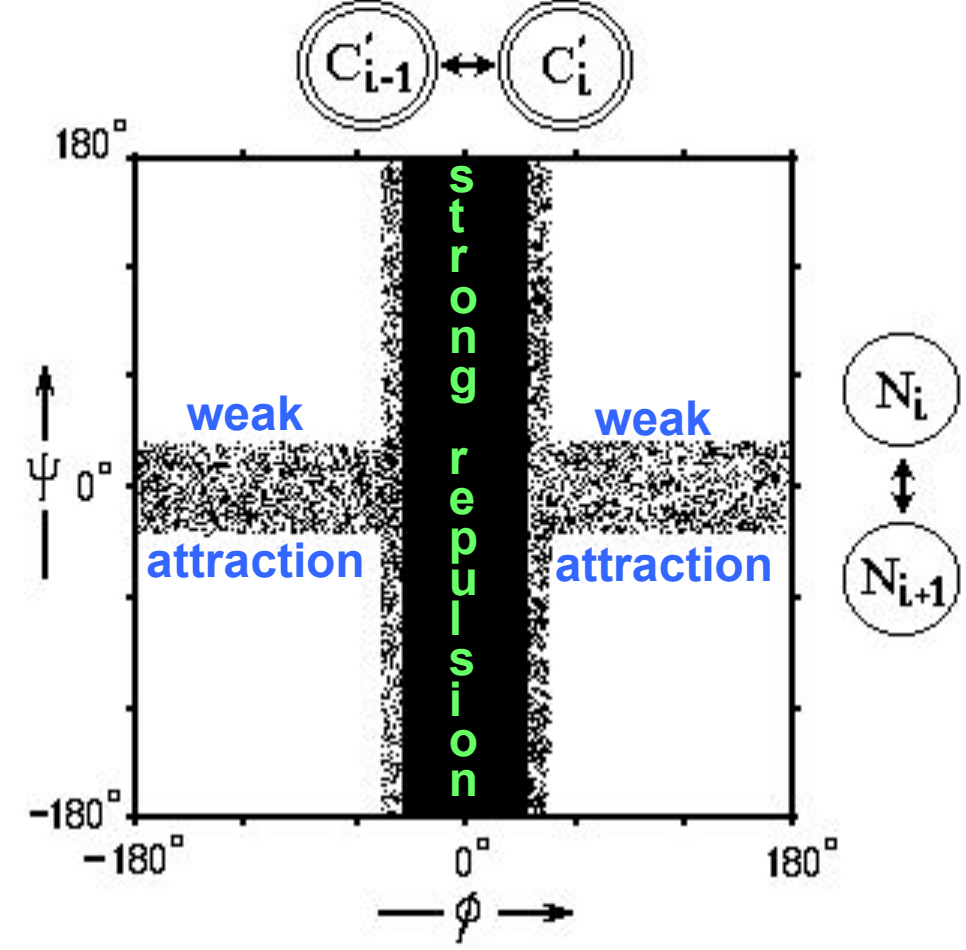
Main-chain:

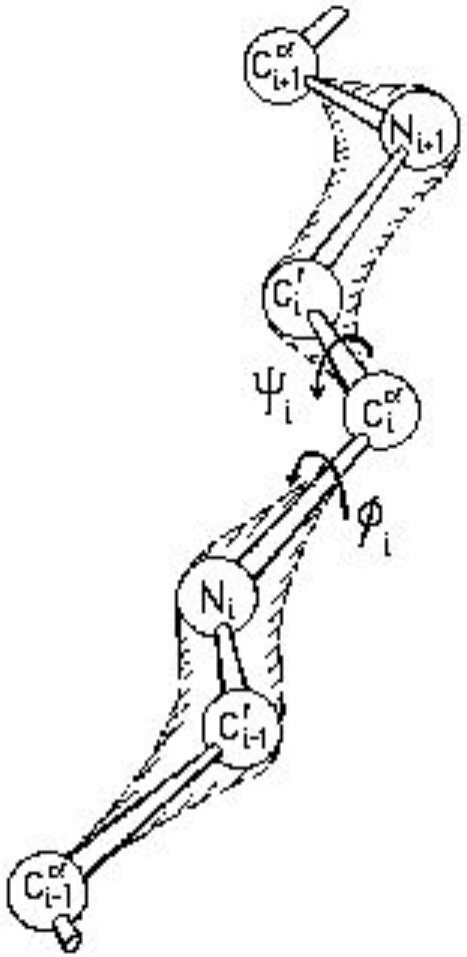
φ (N-Cα) ,

ψ (Cα-C')



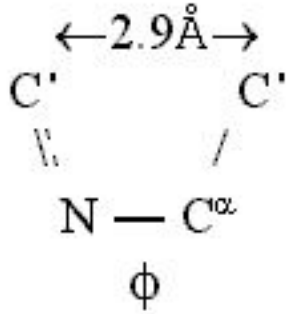
2.8A < r_{min}(C…C) = 3.0A
strong repulsion

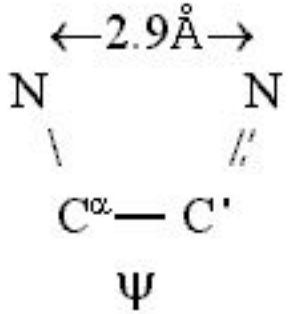




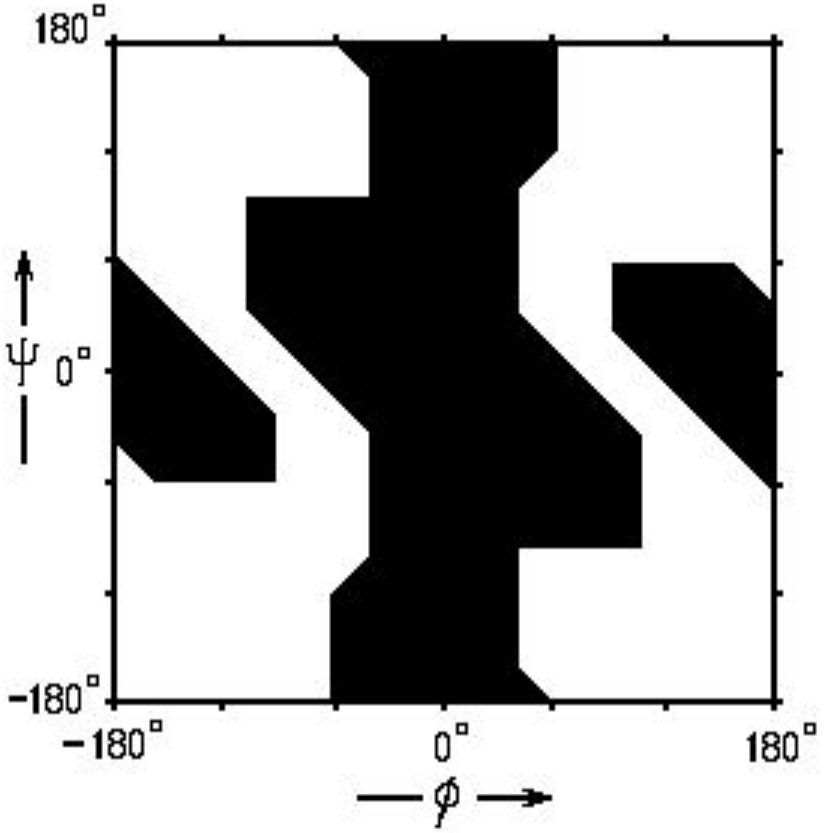
$2.9Å < r_{min}(C...C)=3.0Å$

$2.9Å > r_{min}(N...N)=2.7Å$

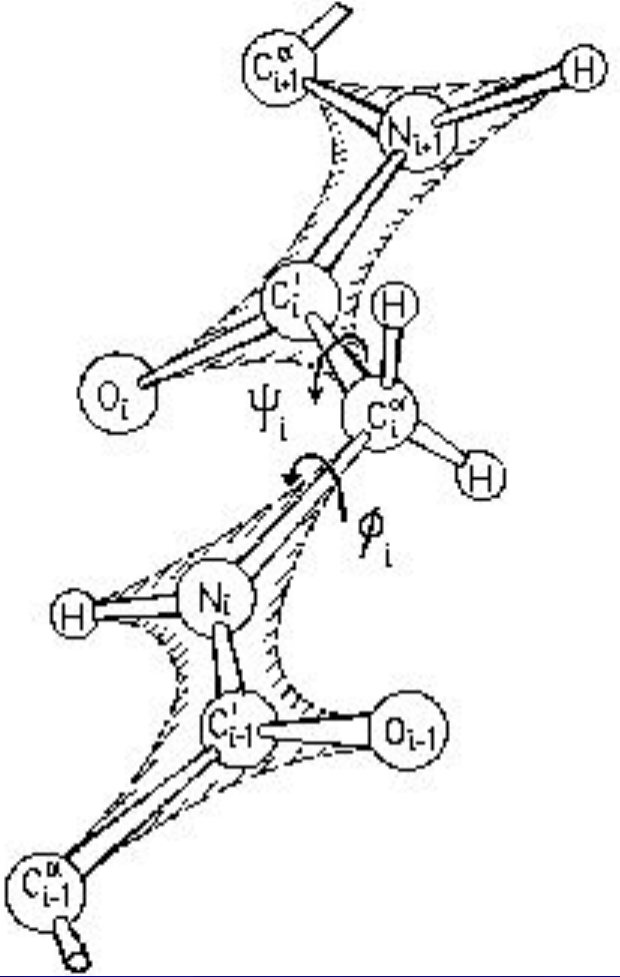


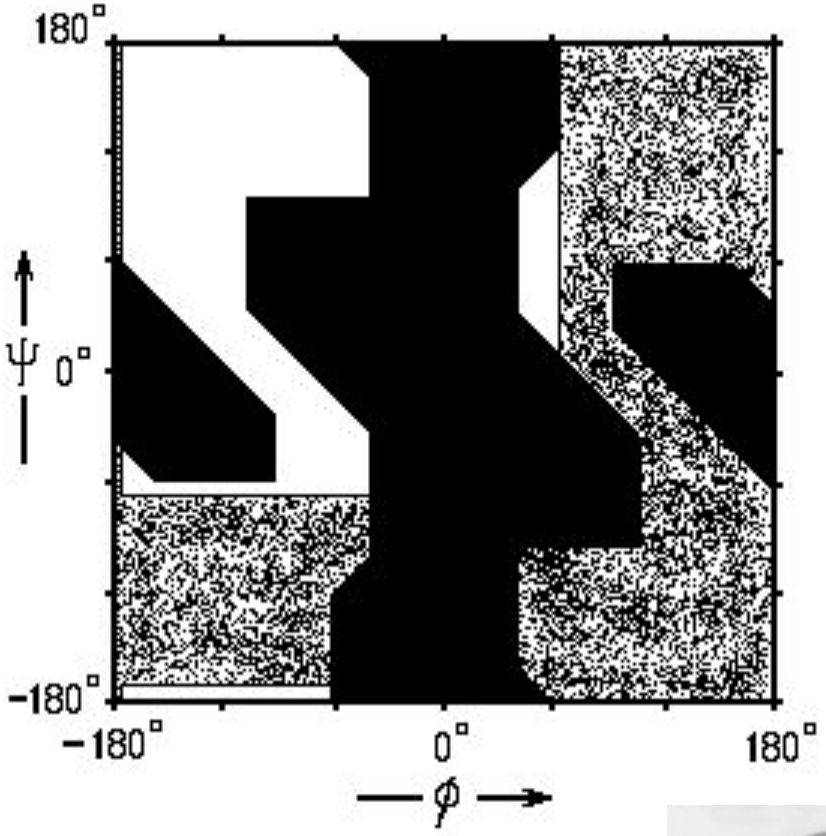


$r_0(N...N)=3.1A$

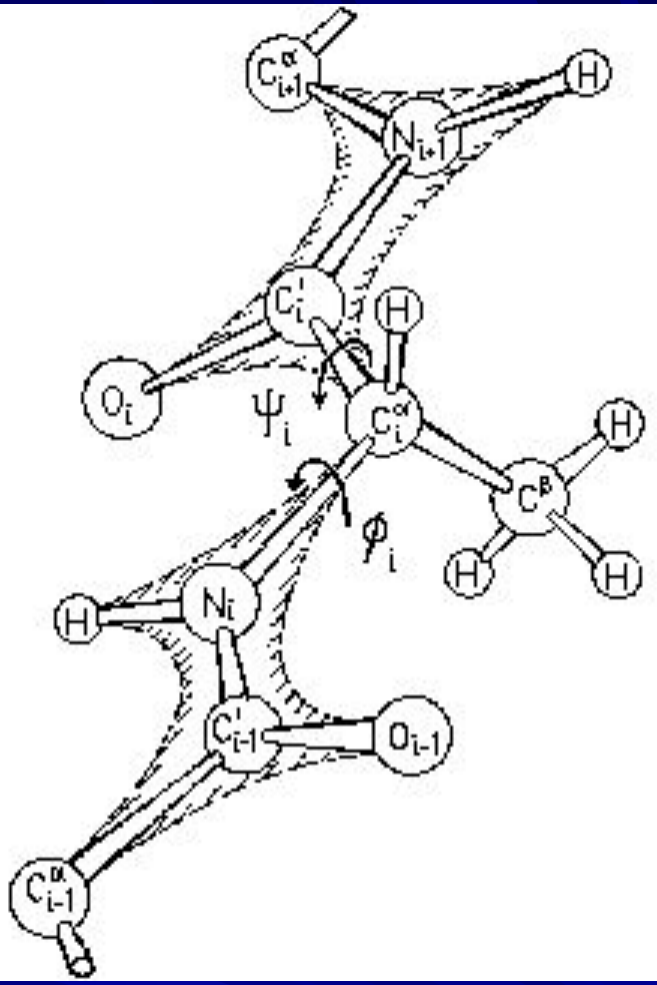

180°
ψ 0°
−180°
−180°
0°
180°
φ

GLY

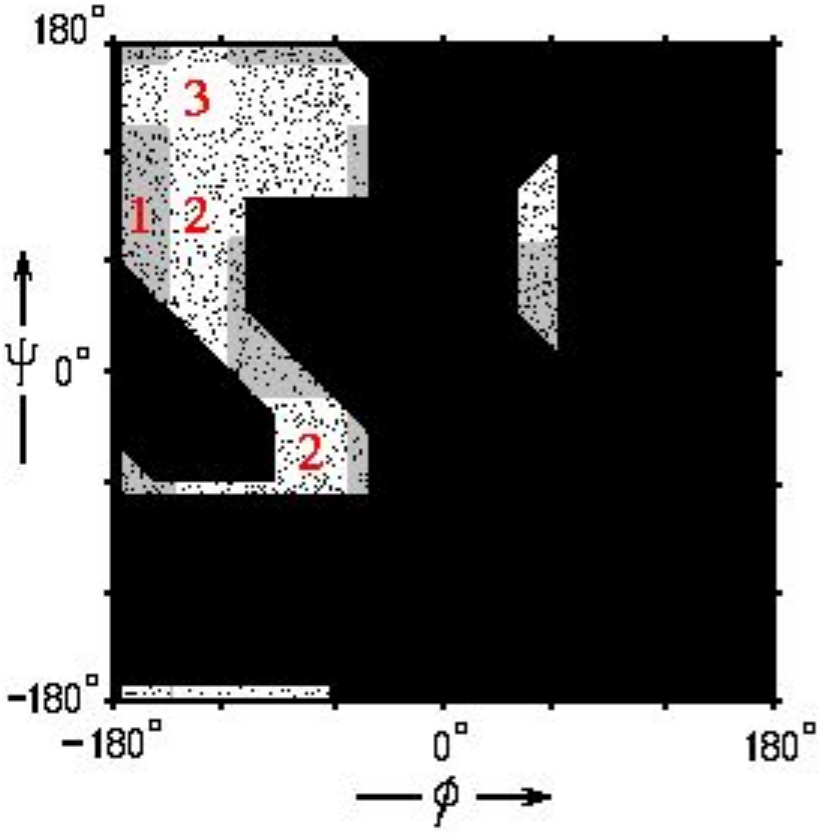

C^{α}_{i+1}
H
N_{i+1}
C'_i
H
O_i
ψ_i
C^{α}_i
H
ϕ_i
H
N_i
C'_{i-1}
O_{i-1}
C^{α}_{i-1}



ALA



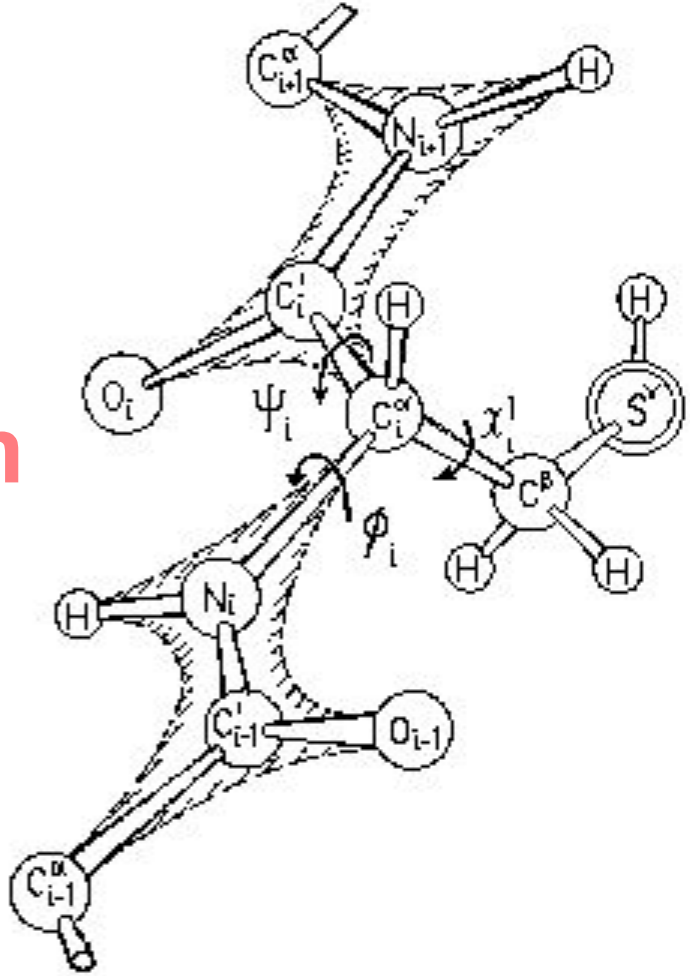
Gopalasamudram Narayana Iyer **Ramachandran**(1922-2001)


180°
3
1
2
2
Ψ
0°
−180°
−180°
0°
180°
φ

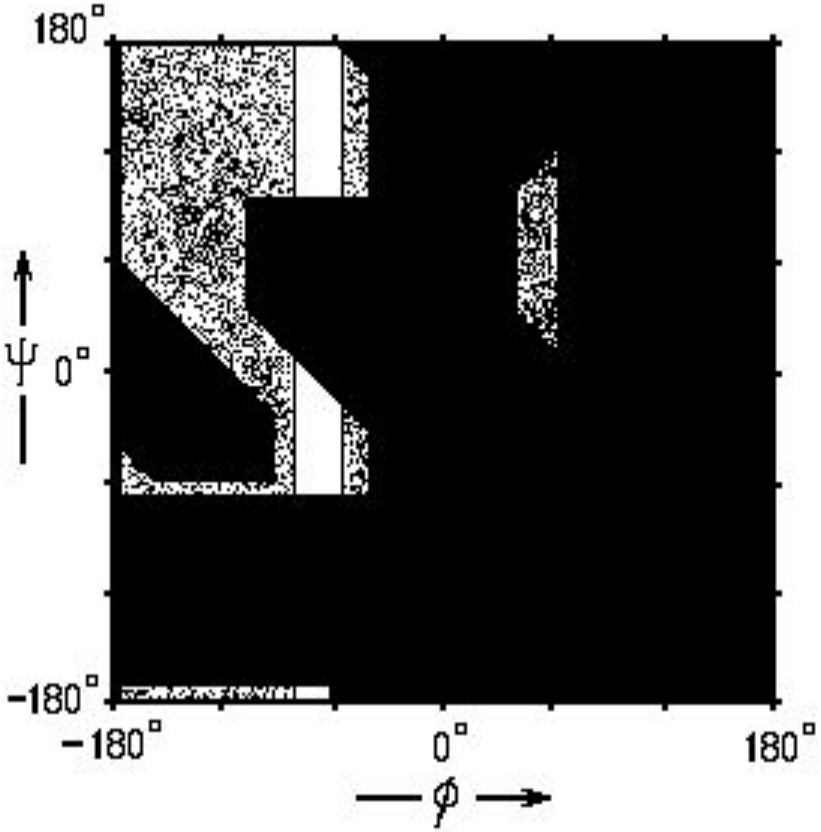
>ALA:

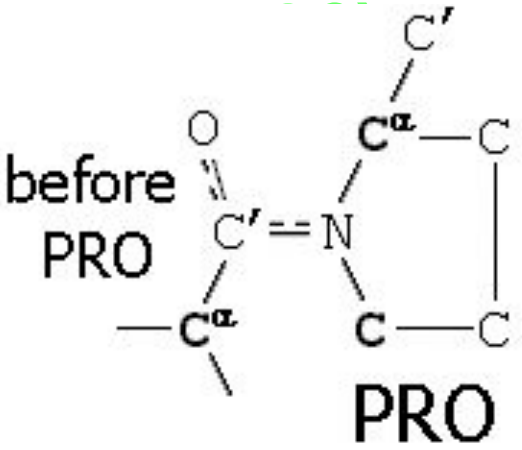
γ-atom

s

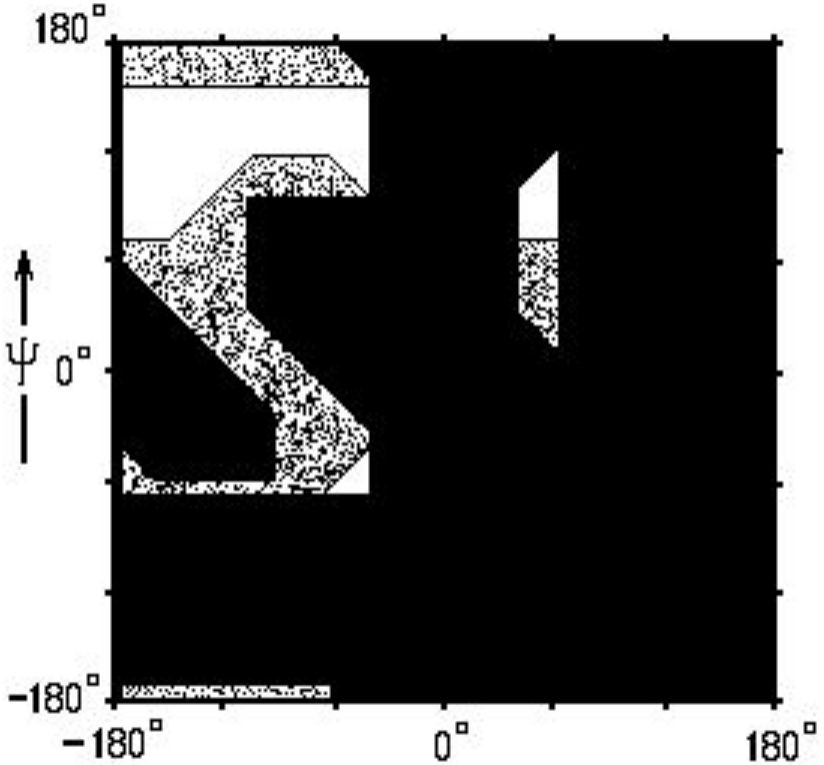

C^{α}_{i+1}
H
N_{i+1}
C'_i
H
H
O_i
Ψ_i
C^{α}_i
χ^1_i
S^{γ}
C^{β}
ϕ_i
H
H
H
N_i
C'_{i-1}
O_{i-1}
C^{α}_{i-1}

PRO (φ =

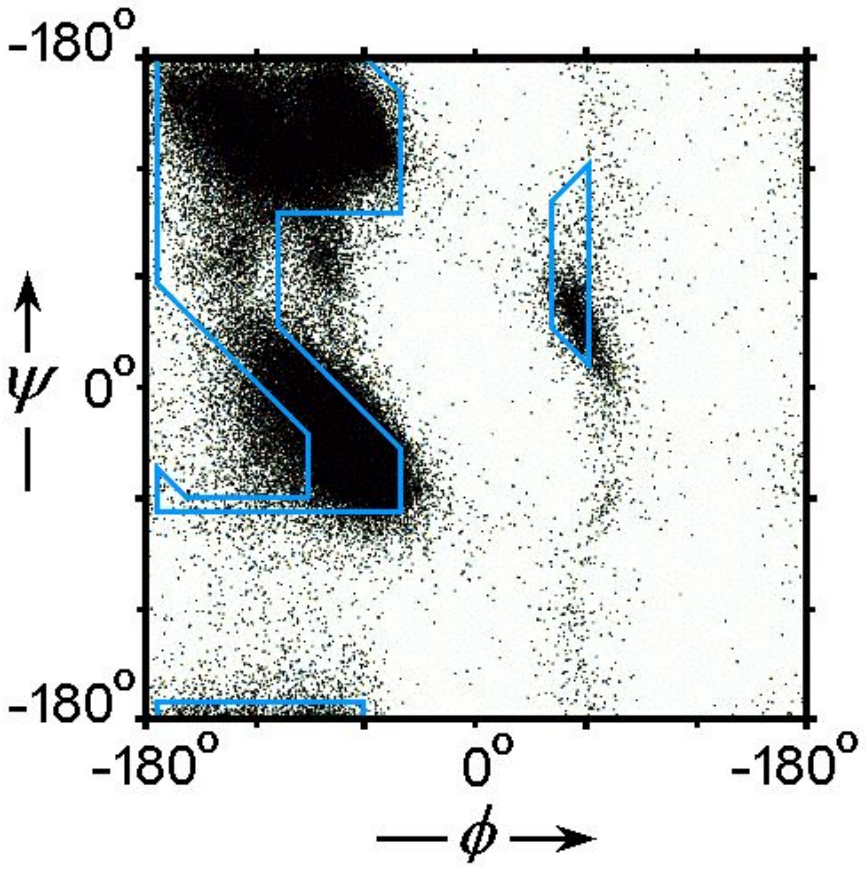




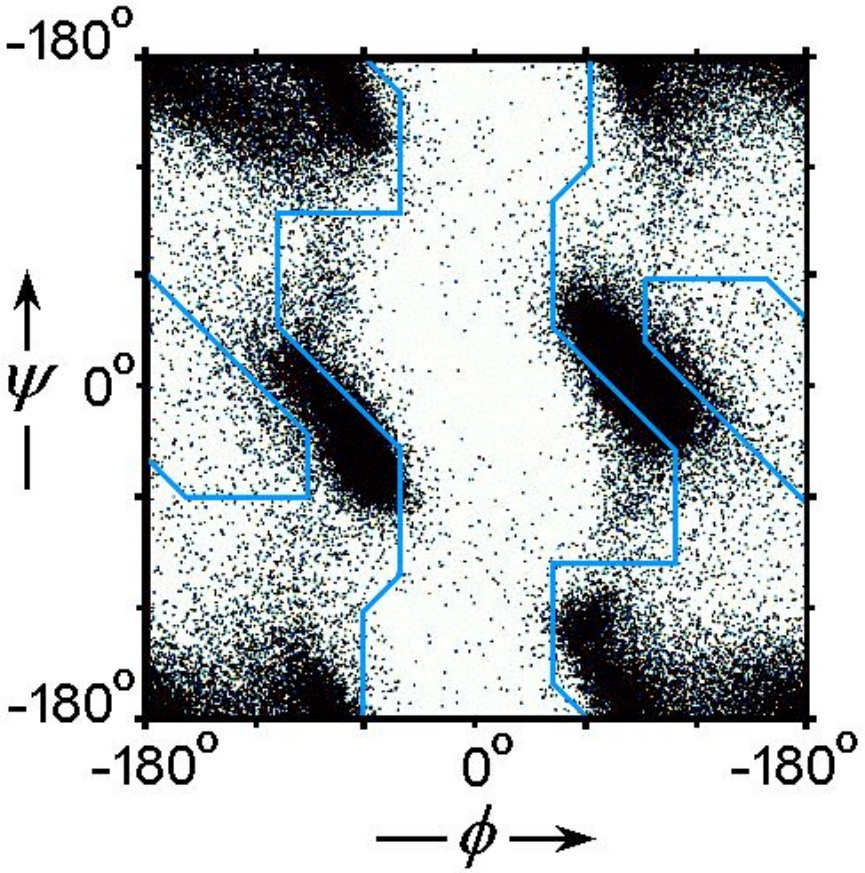
Before PRO



ALA, etc.

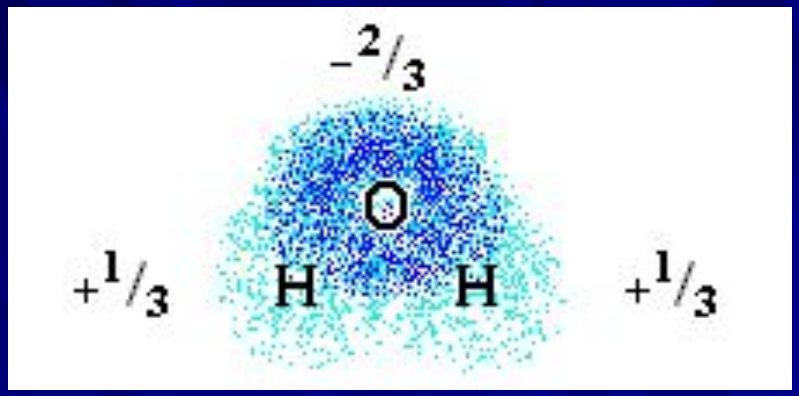


GLY only



HYDROGEN BONDS

WATER molecule:



H-bond energy: 5 kcal/mol

ICE sublimation: (12 kcal/mol - 2 kcal/mol[vdW])/2
10 kcal/mol[CH_3-CH_2-OH] - 5 kcal/mol[CH_3-O-CH_3]

$$U = q_1 q_2 / r$$

$$\varepsilon = e \cdot e / 1\text{Å} = 330 \text{ kcal/mol}$$

$(HO)^{-1/3}$-$H^{+1/3}$ ::::: $O^{-2/3}$-$H_2{}^{+2/3}$: $\varepsilon \cdot {}^{1}/_{3} \cdot {}^{2}/_{3} \cdot (-{}^{1}/_{2} - {}^{1}/_{4} + 2 \cdot {}^{1}/_{3})$
~ 6 kcal/mol

←1.8Å→	←1.9Å→	←2.1Å→
O—H::::::O	N—H::::::O	N—H::::::N
← 2.8Å →	← 2.9Å →	← 3.1Å →

HYDROGEN BONDS

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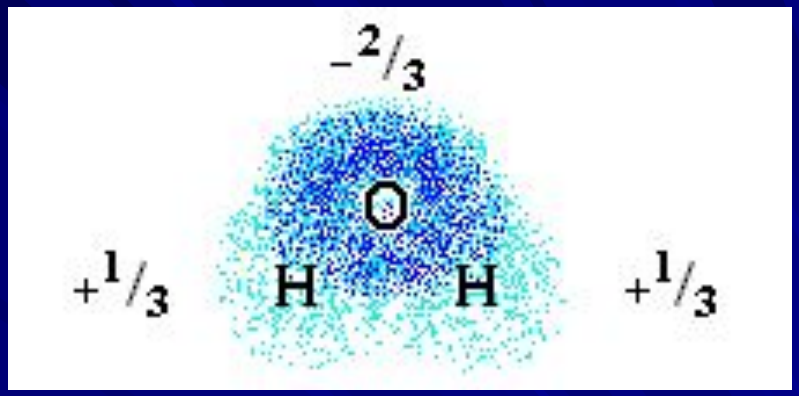

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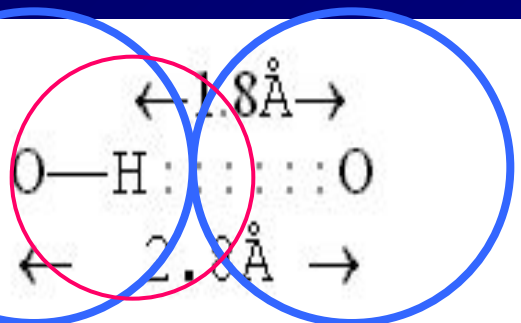
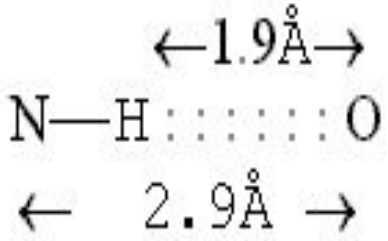
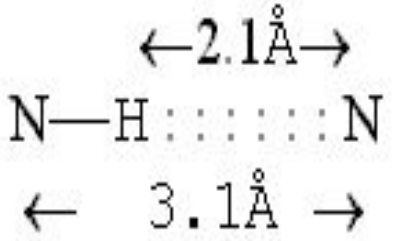
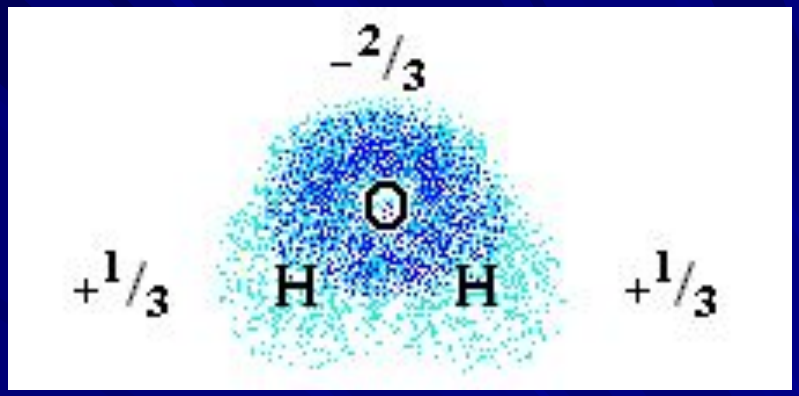






HYDROGEN BONDS

WATER molecule:



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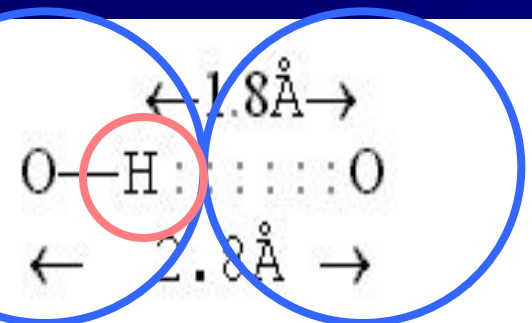
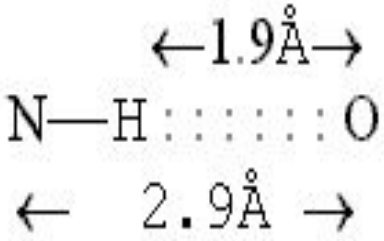
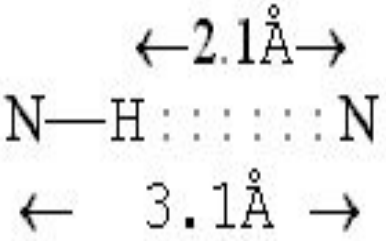
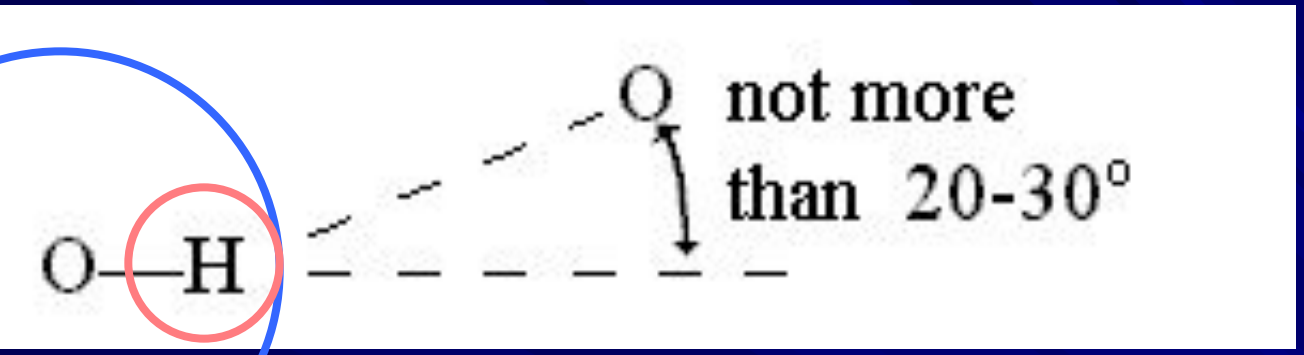
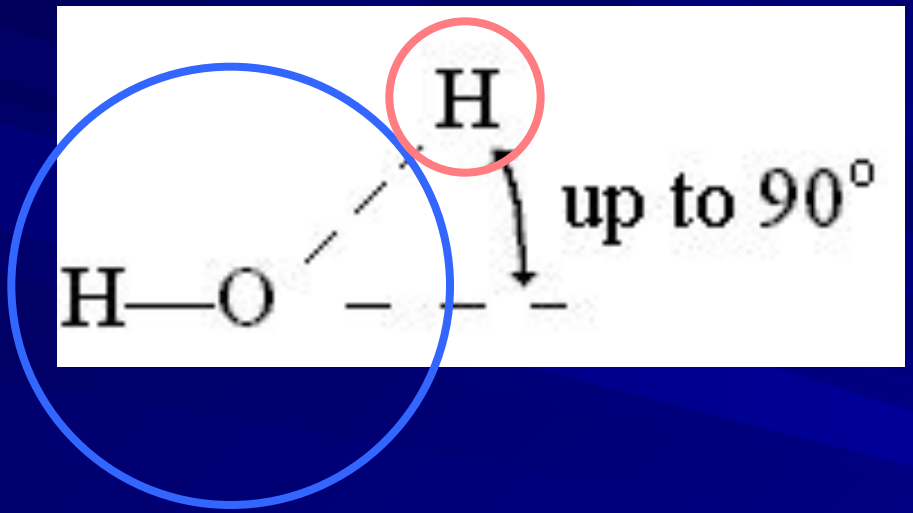
$(HO)^{-1/3}$-$H^{+1/3}$ ::::: $O^{-2/3}$-$H_2^{+2/3}$: $\varepsilon \cdot {}^{1}/_{3} \cdot {}^{2}/_{3} \cdot (-{}^{1}/_{2} - {}^{1}/_{4} + 2 \cdot {}^{1}/_{3})$
~ 6 kcal/mol

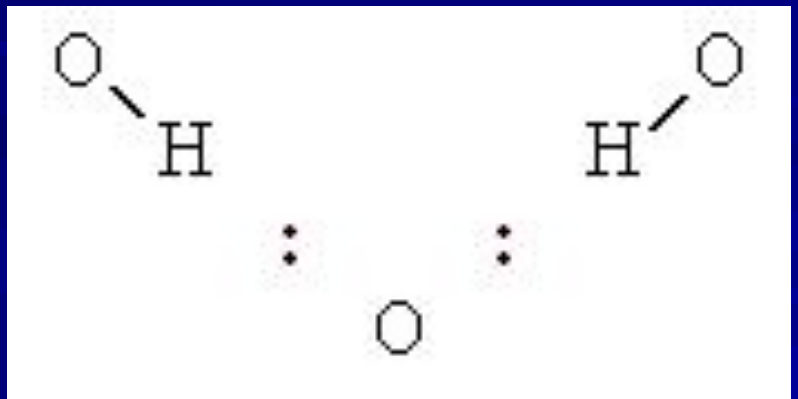


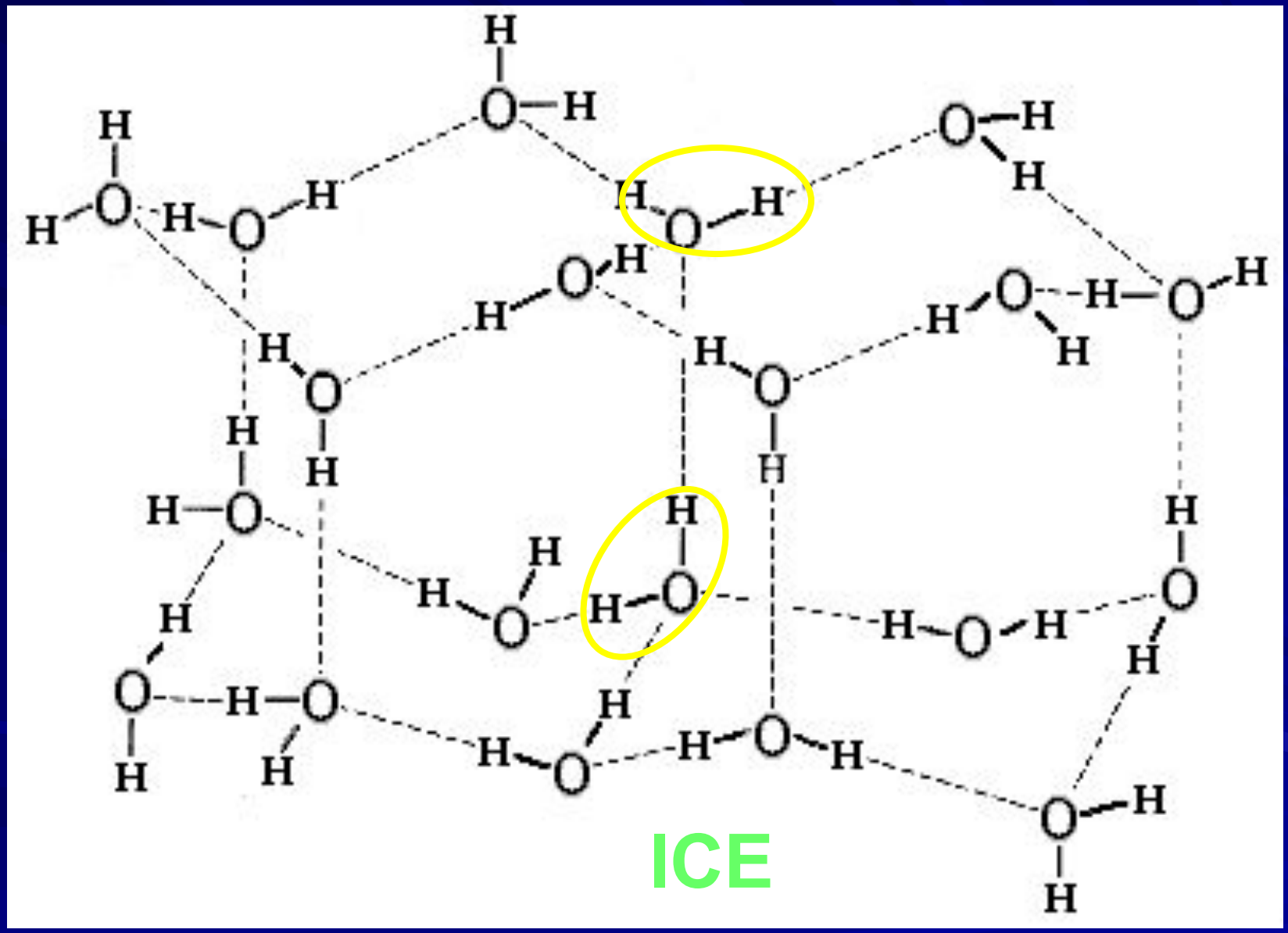




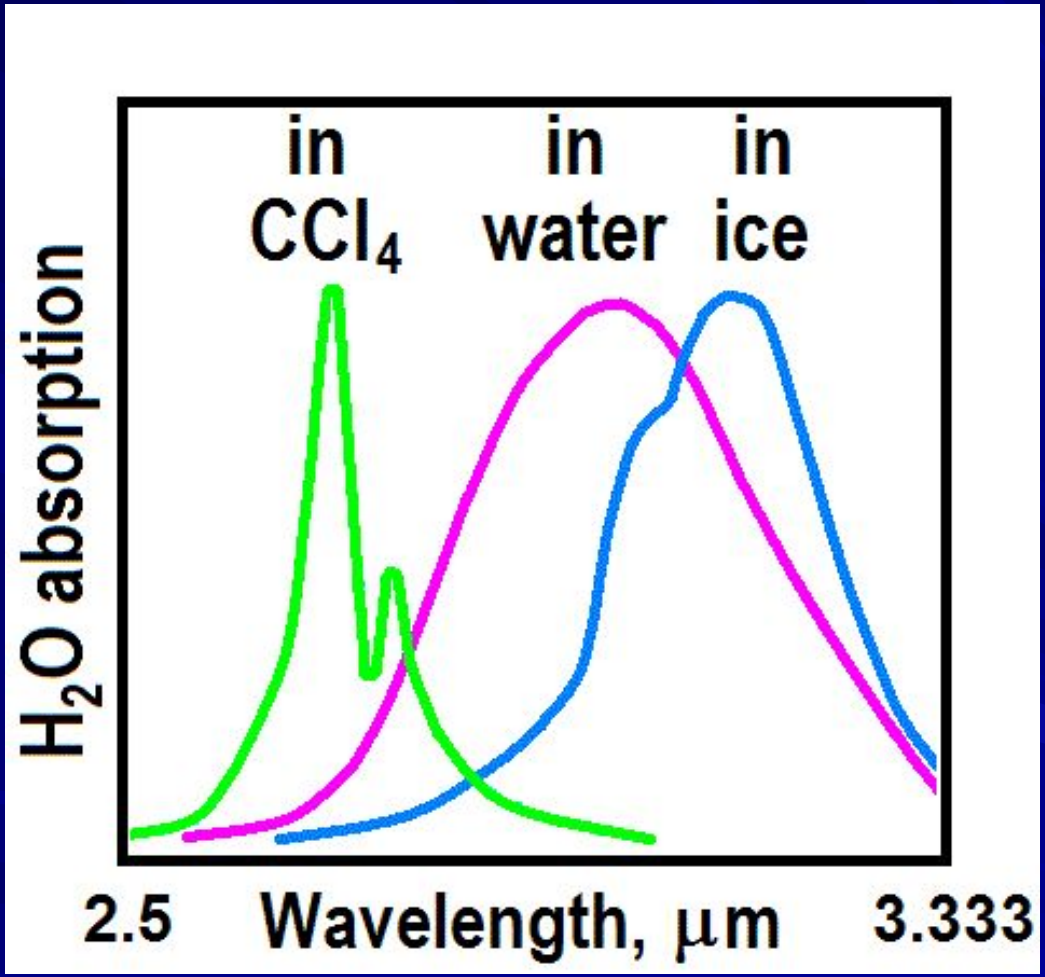

O
not more
than 20-30°
O—H


H
up to 90°
H—O


O
H
H
O
O


ICE

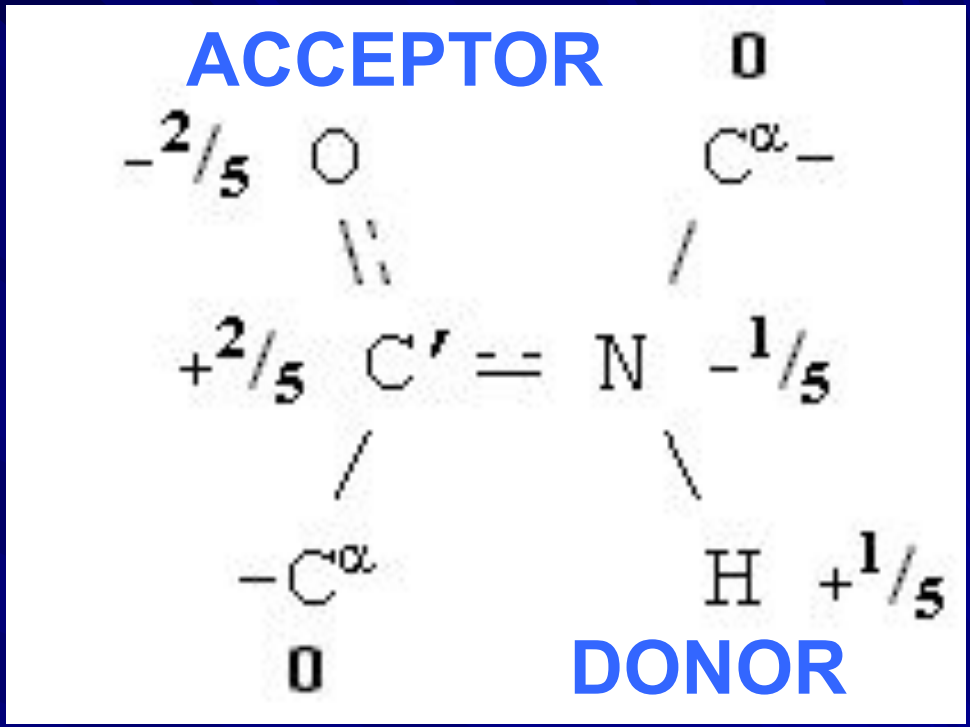
MODEL OF "FORMED" and "BROKEN" H-BONDS IN WATER IS VERY ROUGH



O-H

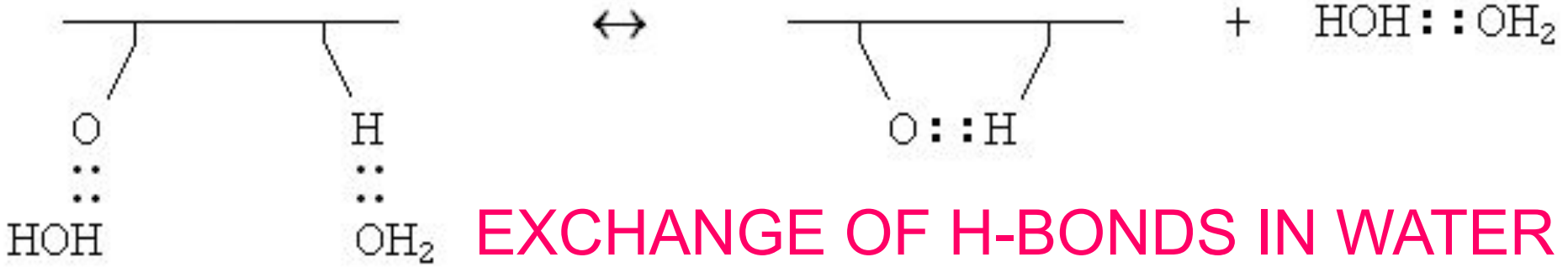
O--H ::: O

PEPTIDE GROUP ALSO FORMS H-BONDS



FORMATION OF H-BOND IN VACUUM

ENERGY **E** *decreases*



EXCHANGE OF H-BONDS IN WATER

ENERGY **E** = *const* ENTRORY **S**~ln(pos.) *increases*

FREE ENERGY **F=E-TS** *decreases*: water moves

Just because H-bonds have large energy, only their ENTROPIC part plays a role in water surrounding