Core-ionized and core-excited states of macromolecules

Pierre-François Loos Xavier Assfeld

Equipe de Chimie et Biochimie Théoriques
UMR 7565 CNRS-UHP, Institut Jean Barriol (FR CNRS 2843)
Faculté des Sciences et Techniques, Nancy-Université
France

March 2, 2007

Core Electron Binding Energies (CEBEs)

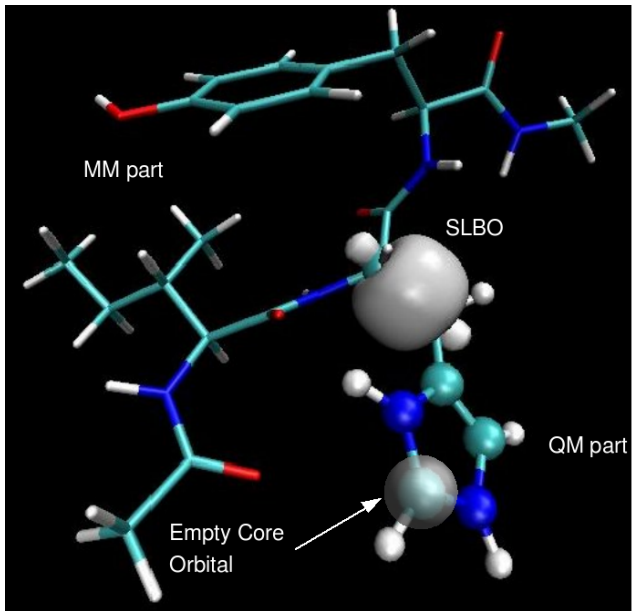
- Useful tools to obtain information on the structure and on the nature of molecules[a]
- Experimental studies on macromolecules[b]

[a] Schwarz et al. Angew. Chem. Int. Ed. 1974, 13, 454.
[b] see for example : Gordon et al. J. Phys. Chem. A 2003, 107, 8512.

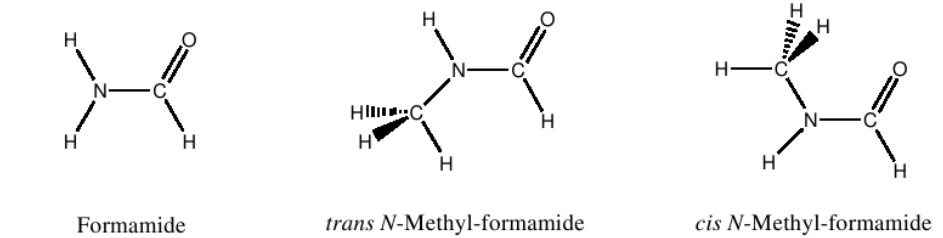
Theoretical Study

- Excited States $\Longrightarrow$ variationnal collapse and orthogonality constraint[a]
- Macromolecular systems $\Longrightarrow$ QM/MM within the LSCF method[b]

[a] Ferré et al. J. Chem. Phys. 2002, 117, 4119.
[b] Assfeld et al. Chem. Phys. Lett. 1996, 263, 100.



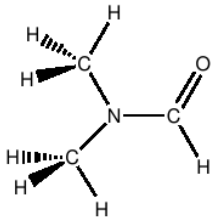
Core-ionized states of the peptide bond: C 1s CEBEs PBE0/6-311++G**//B3LYP/6-311++G**



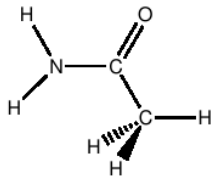
Formamide

trans N-Methyl-formamide

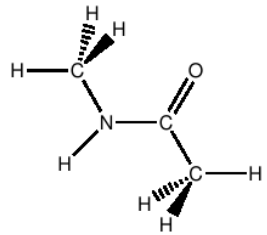
cis N-Methyl-formamide



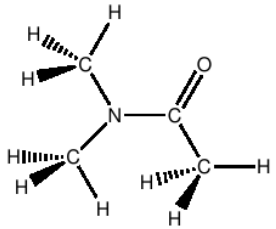
N,*N*-Dimethyl-formamide



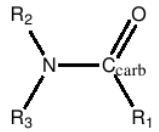
Acetamide



N-Methyl-acetamide



N,*N*-Dimethyl-acetamide



Atom Label

C_{carb} Formamide

- Exp.[a]: 294.45 eV
- Ref.[b]: 294.16 eV (+0.29)
- This work: 294.41 eV (+0.04)

[a] Joly et al. J. Atomic Data and Nuclear Data Tables, 1984, 31, 433.
[b] Chong et al. J. Phys. Chem. A 2002, 106, 356.

C_{carb}, C_{R2}, C_{R3} N,N-dimethylformamide

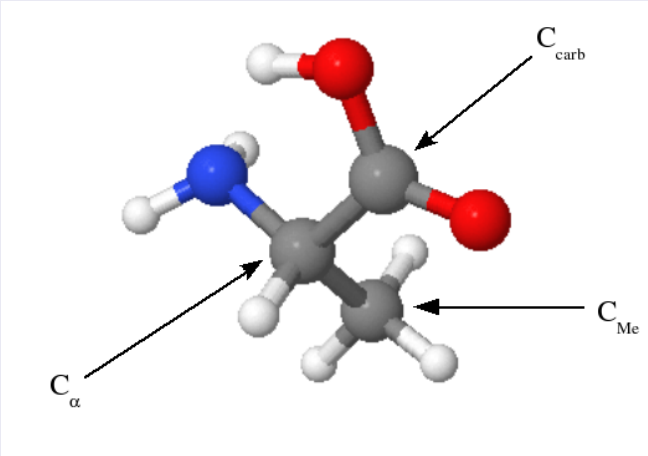
- Exp.: 293.45, 292.03, 292.03 eV
- Ref.: 293.25(+0.20), 291.92(+0.11), 292.27(-0.24) eV
- This work: 293.52(-0.07), 291.86(+0.17), 292.24(-0.21) eV

Maximum deviation Theory vs Theory & Exp. vs Theories

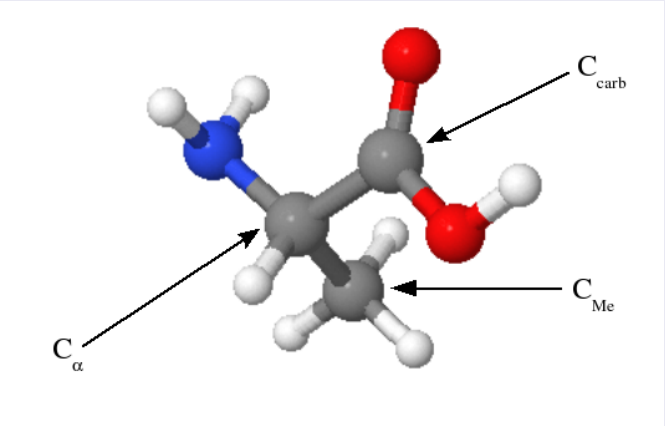
- Ref.-This work: $\simeq 0.3$ eV
- Exp.-This work: $\simeq 0.2$ eV
- Exp.-Ref.: $\simeq 0.2$ eV

$\Longrightarrow$ Accurate carbon 1s ionization energies w.r.t Theory and Exp.

Conformations: $\Delta E < 1$ kcal/mol



(a) Conf. 1



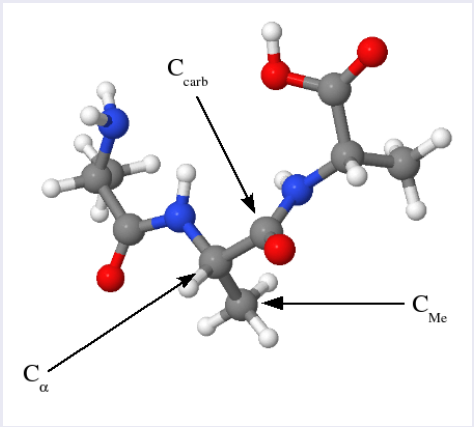
(b) Conf. 2

Alanine CEBEs (eV)

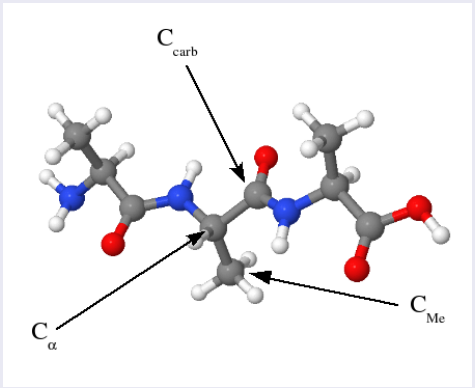
	conf. 1	conf. 2	Exp.[a]
C_α	292.45(-0.15)	292.16(+0.14)	292.30
C_{carb}	294.60(+0.70)	294.92(+0.38)	295.30
C_{Me}	291.11(+0.09)	290.89(+0.31)	291.20

[a] Powis et al. J. Phys. Chem. A 2003, 107, 25.

Ala-Tripeptide: α-helix and β-sheet conformations



(c) α-helix



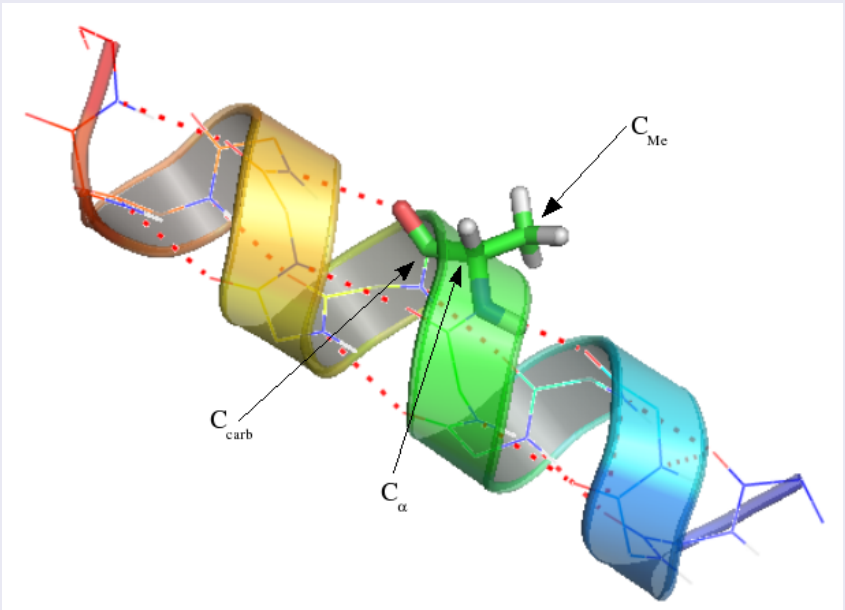
(d) β-sheet

Ala-Tripeptide CEBEs (eV)

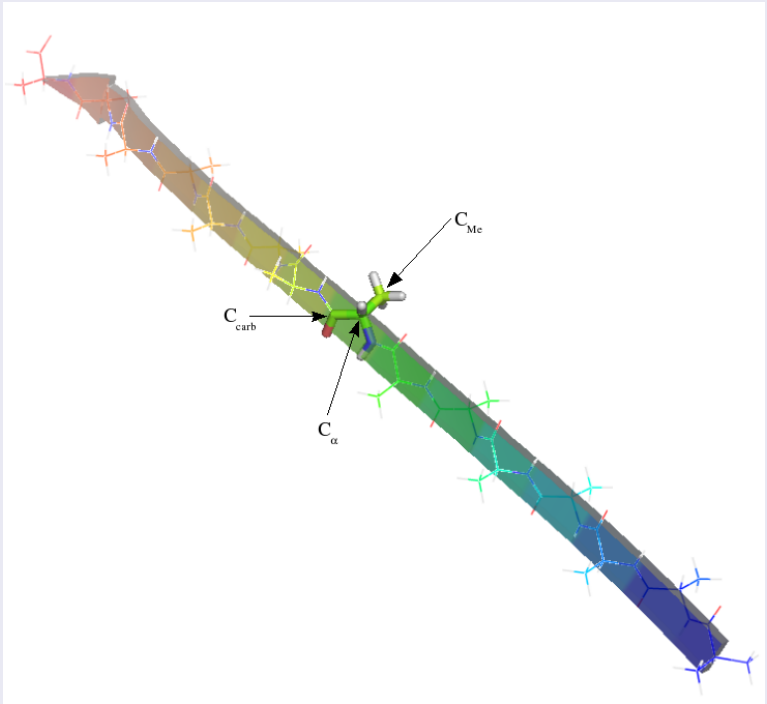
	α-helix	β-sheet	
C_α	291.87	292.00	$\simeq$ 0.3-0.4 eV
C_{carb}	293.69	293.87[a]	$\simeq$ 2.0 eV
C_{Me}	290.50	290.62	$\simeq$ 0.3-0.4 eV

[a] C_{carb} N-methylacetamide 293.37 eV

poly-Ala-pentadecapeptide

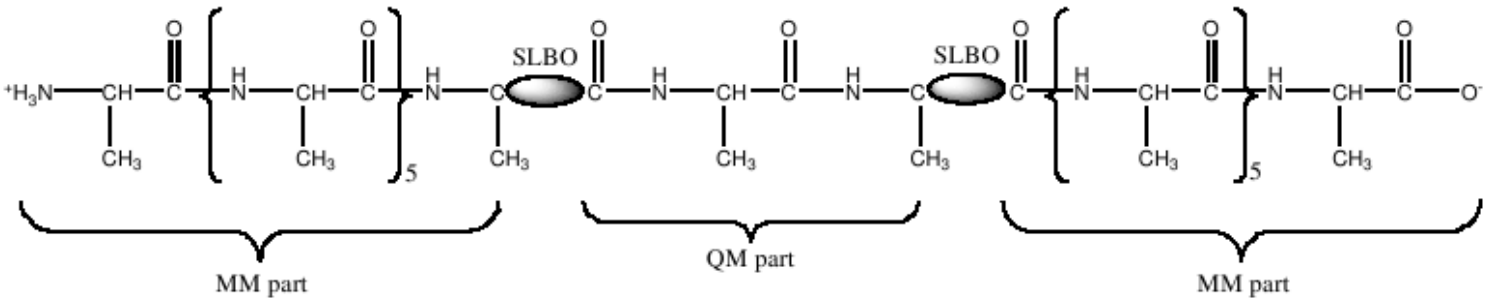


(e) α-helix



(f) β-sheet

QM/MM partition of the poly-Ala-pentadecapeptide



Pentadecapeptide CEBEs (eV)

	PBE0/Amber		PBE0/Amber*[a]	
	α-helix	β-sheet	α-helix	β-sheet
C_{α}	-0.26	-0.62	+0.05	+0.08
C_{carb}	-0.09	-0.76	+0.63	+0.23
C_{Me}	-0.71	-0.32	+0.47	+0.11

[a]The Amber* calculations are performed excluding the electrostatic polarization of the wave function by the classical point charges

Conclusions

- Orthogonality between GS and ES
- Accurate carbon 1s ionization energies :
  PBE0/6-311++G**//B3LYP/6-311++G** + Boys-Foster CO
- Carbon 1s ionization energies sensible to:
  - Chemical shift (closest surroundings)
  - Polarization (long-range interactions) 0.2-1.0 eV

Outlooks

Extension to the innershell absorption spectra

- Most common proteinogenic α-amino acids
- Experimental NEXAFS spectra available
  Kaznacheyev et al. J. Phys. Chem. A, 2002, 106, 3153
  Zubavichus et al. J. Phys. Chem. A, 2005, 109, 6998
- Real biological systems: enzymes, proteins, RNA or DNA