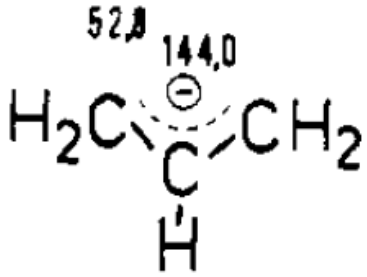
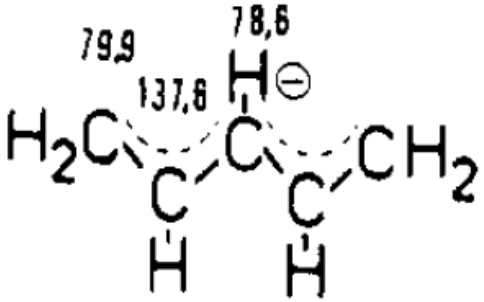
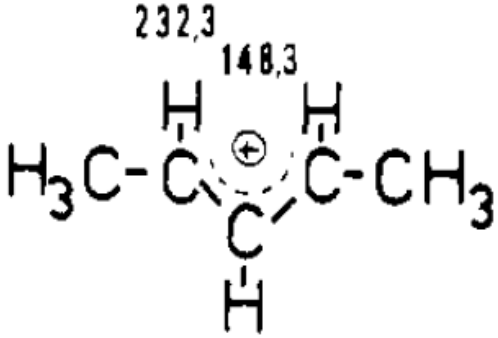
アリルアニオン・アリルカチオンの^{13}C NMR化学シフト (Me_4Si基準，ppm)

^{13}C NMR chemical shifts of allyl cation/anions

(G. Olah et al., *J. Am. Chem. Soc.*, **100**, 4347 (1978))







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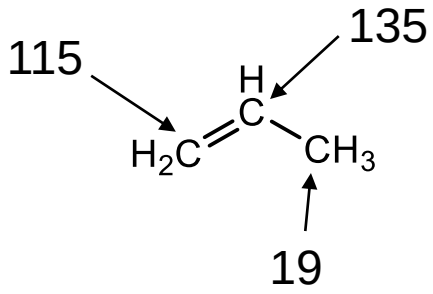

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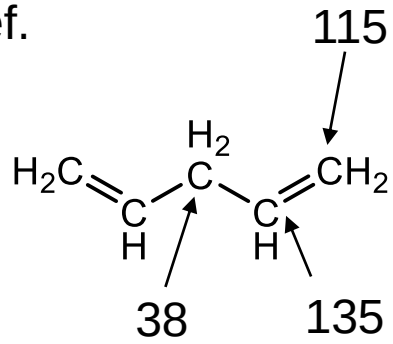

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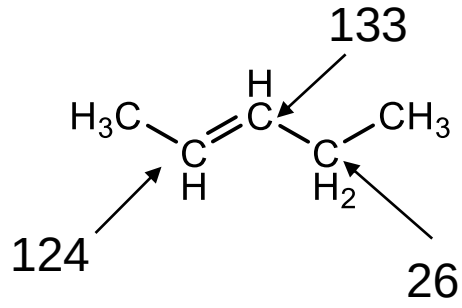
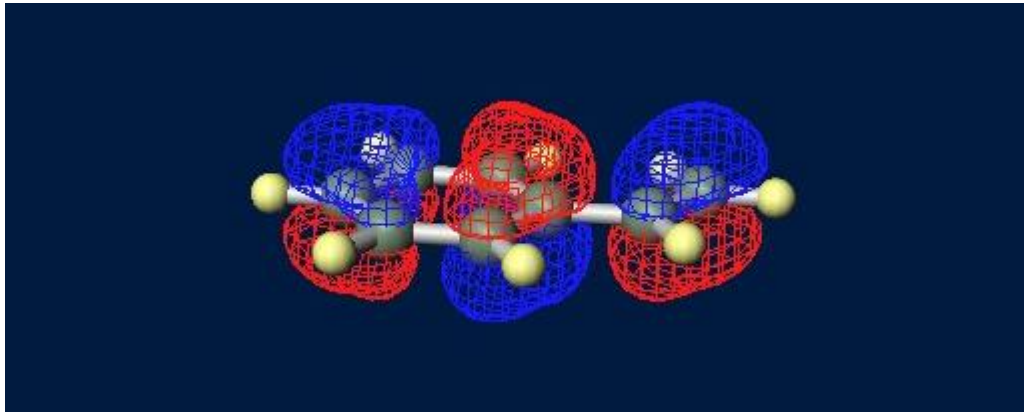


- 両端の等価性，両端と中心炭素の環境の違い，アニオン・カチオンの化学シフト
- Equivalence of two termini. Difference between terminal and center. Chemical shift of cations/anions

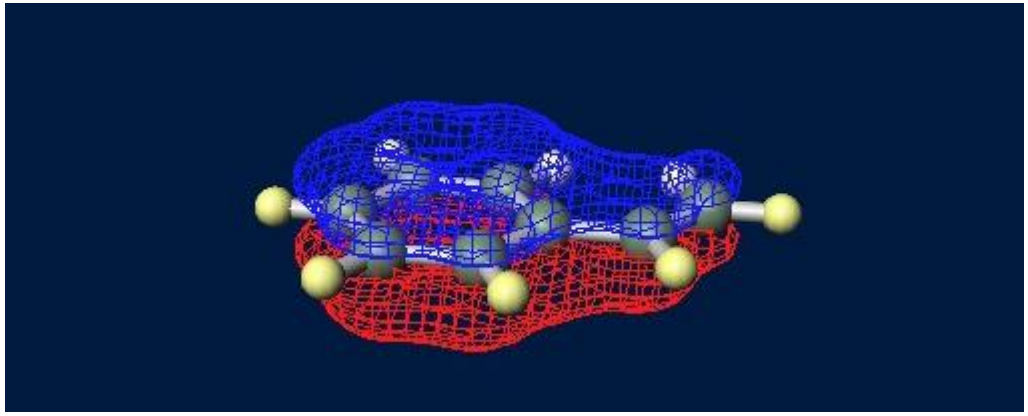
Molecular orbitals with π-character

Styrene C_6H_5-CH=CH_2

HOMO (-9.13 eV)



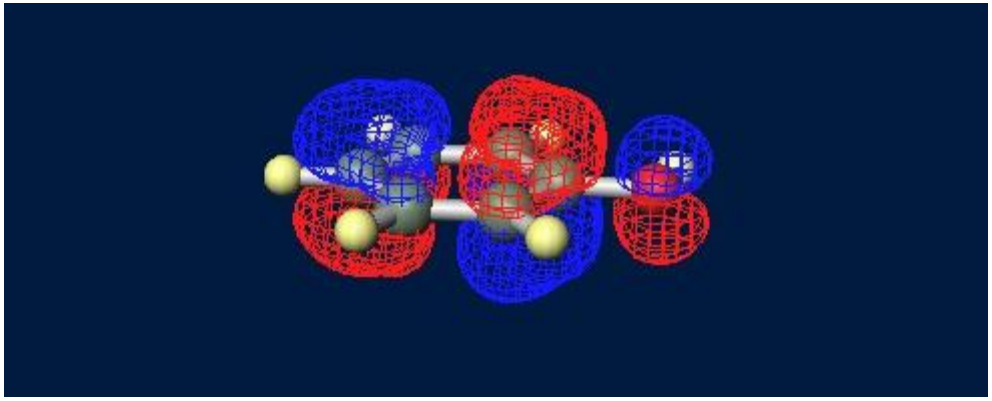
One of other occupied MOs (-13.49 eV)



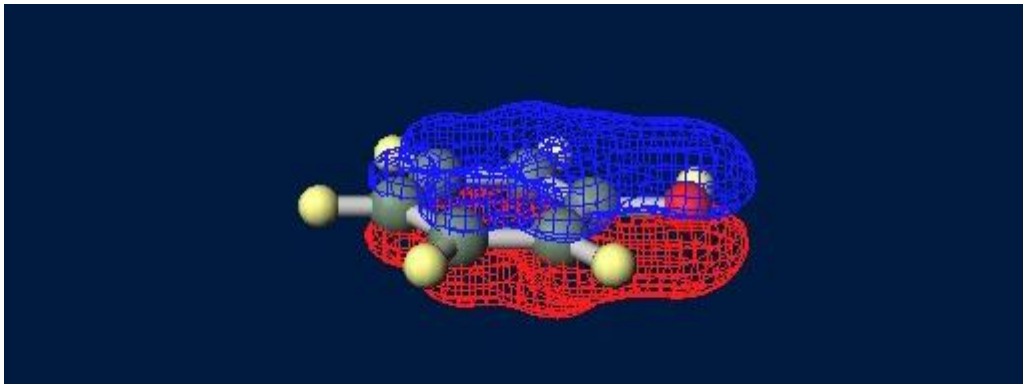
Molecular orbitals with π-character

Phenol C_6H_5-OH

HOMO (-9.17 eV)



One of other occupied MOs (-14.70 eV)

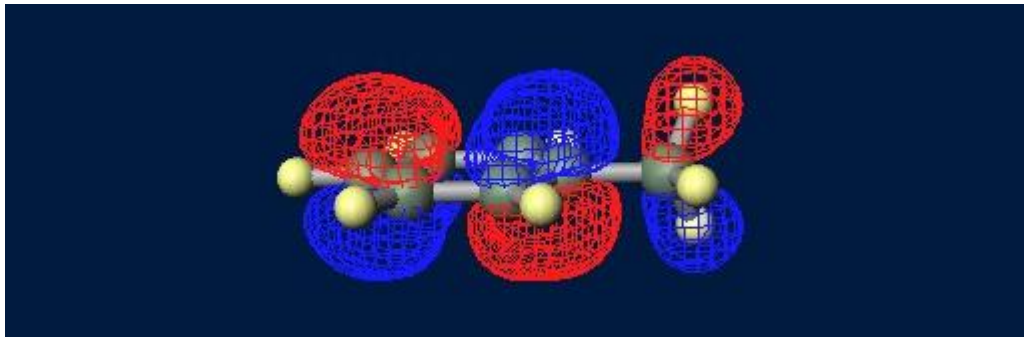


- Oxygen is involved in π-system

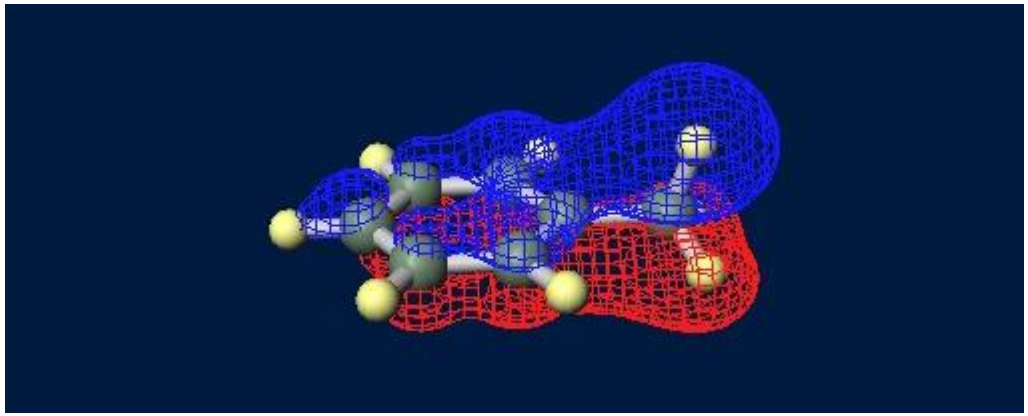
Molecular orbitals with π-character

Toluene C_6H_5-CH_3

HOMO (-9.44 eV)



One of other occupied MOs (-14.57 eV)

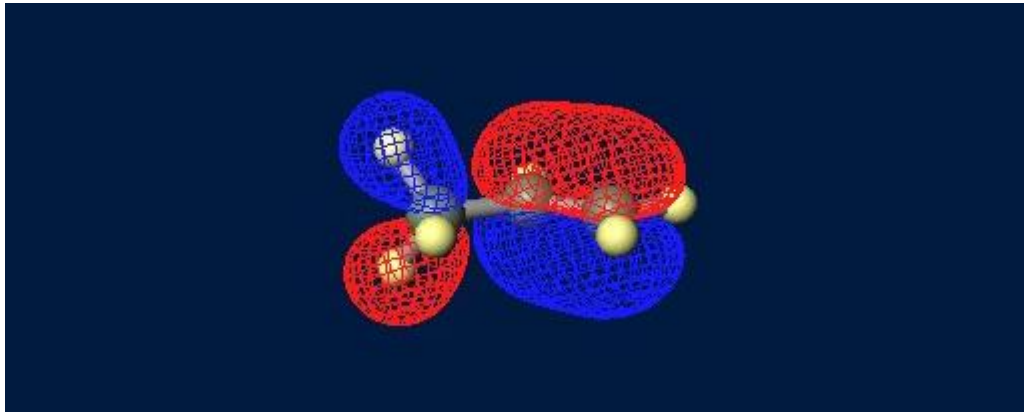


- Methyl group is also involved in π-system !?

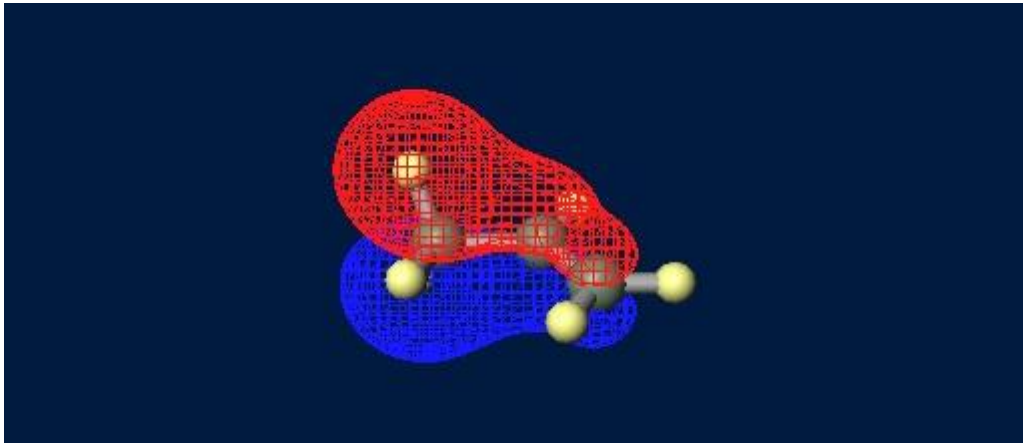
… likewise

propene CH_3-CH=CH_2

HOMO (-10.10 eV)



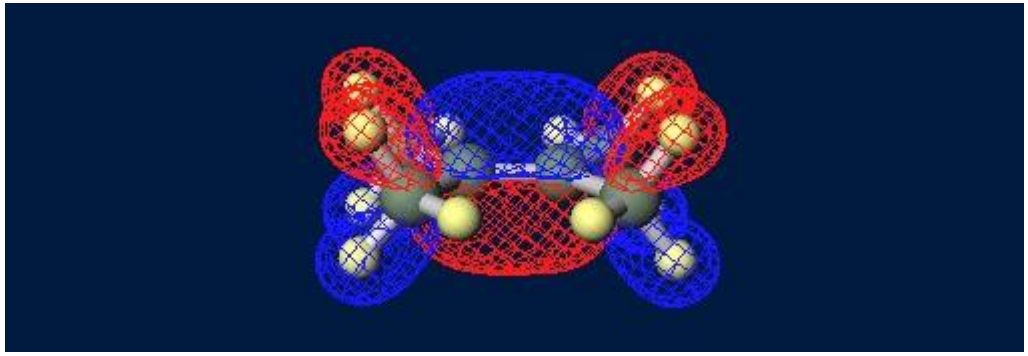
One of other occupied MOs (-14.57 eV)



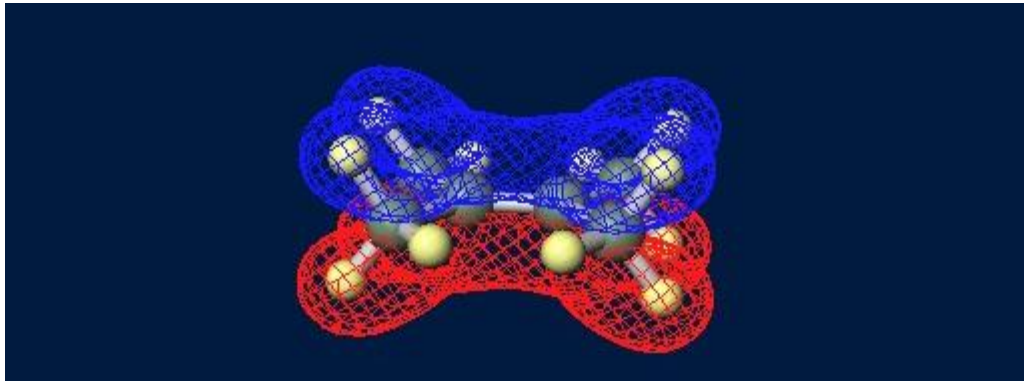
π-system is extended to outer alkyl group!

2,3-dimethylbut-2-ene $(CH_3)_2C=C(CH_3)_2$

HOMO (-9.14 eV)

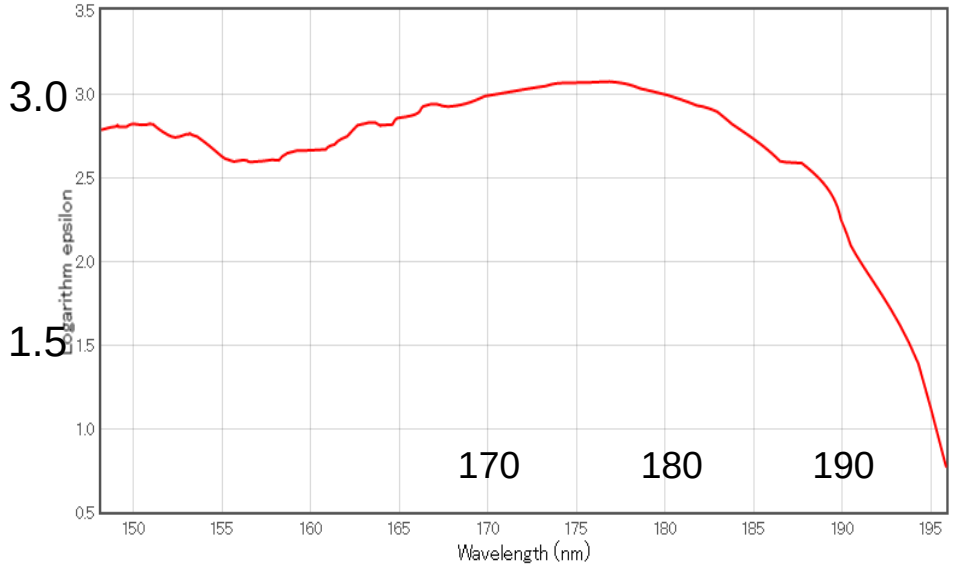


One of other occupied MOs (-15.47 eV)

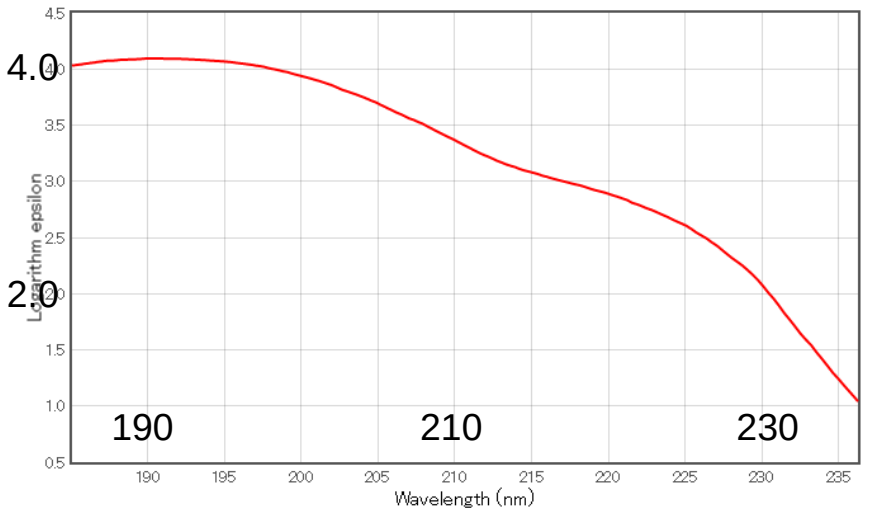


置換アルケンのUV/visスペクトル　UV/vis spectra of substituted alkenes

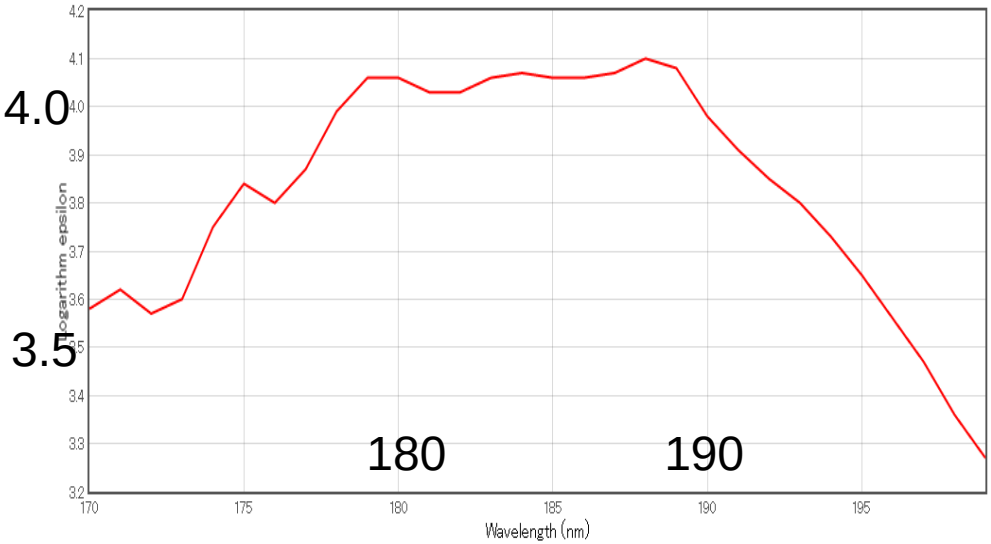
but-1-ene $CH_3CH_2CH=CH_2$



2,3-dimethylbut-2-ene $(CH_3)_2C=C(CH_3)_2$



2-methylpropene $(CH_3)C=CH_2$



アルキルカチオン – 空の2pz軌道への電子供与による非局在化

alkyl cations – delocalization by donation of electrons toward unoccupied 2pz orbital.

methane -13.01 kcal/mol

methyl cation 256.55 kcal/mol

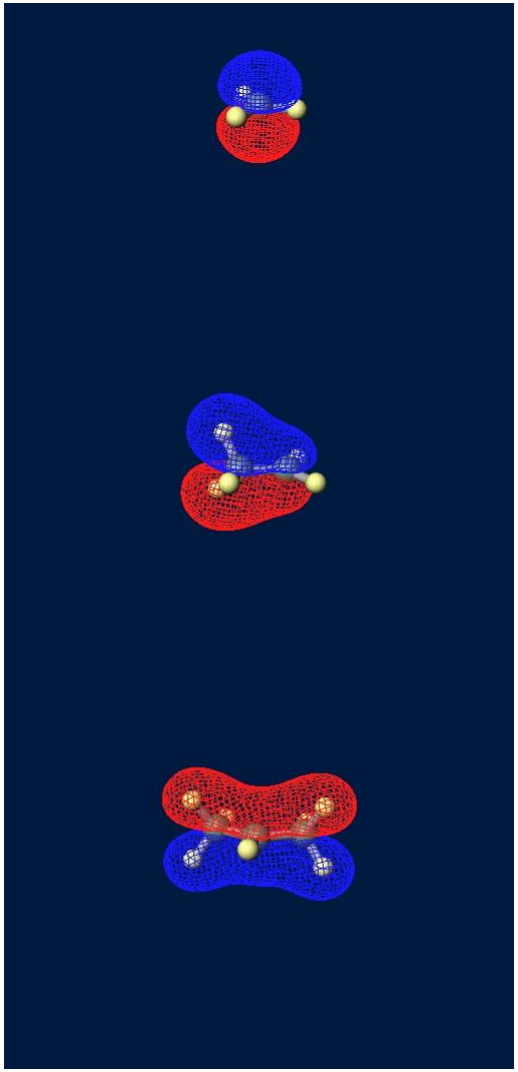
ethane -18.13 kcal/mol

ethyl cation 222.56 kcal/mol

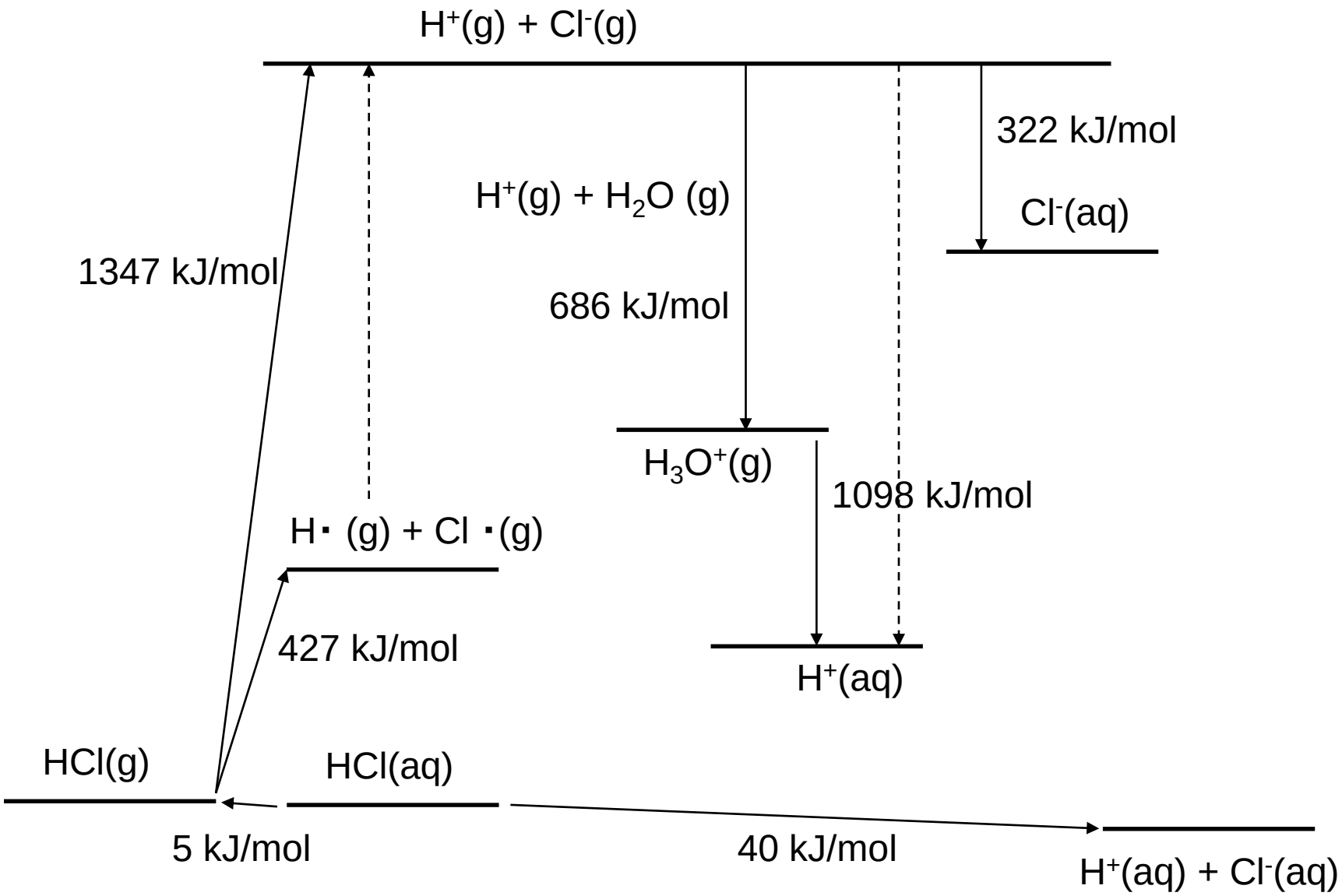
propane -23.62 kcal/mol

2-propyl cation 197.25 kcal/mol

cf. 1-propyl cation 214.36 kcal/mol

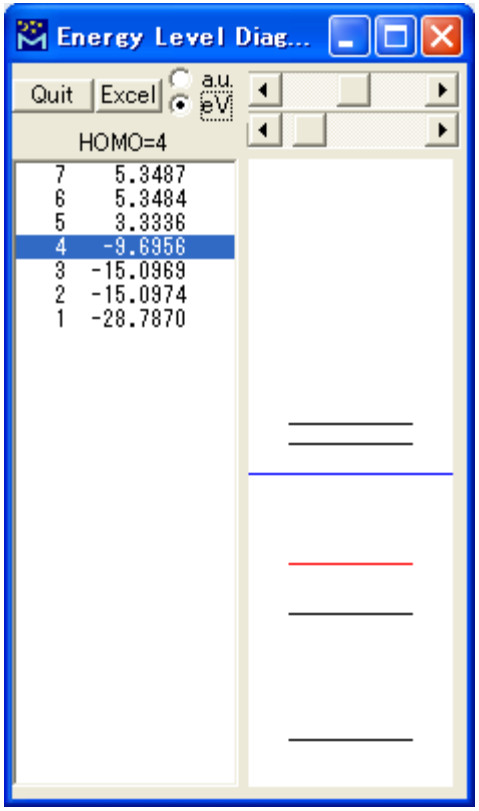


HClの解離と水和エネルギー

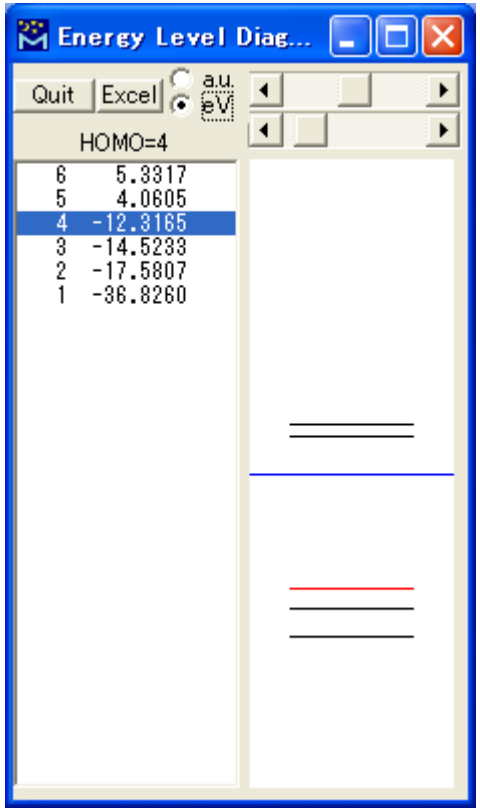


塩基性とHOMOのレベル

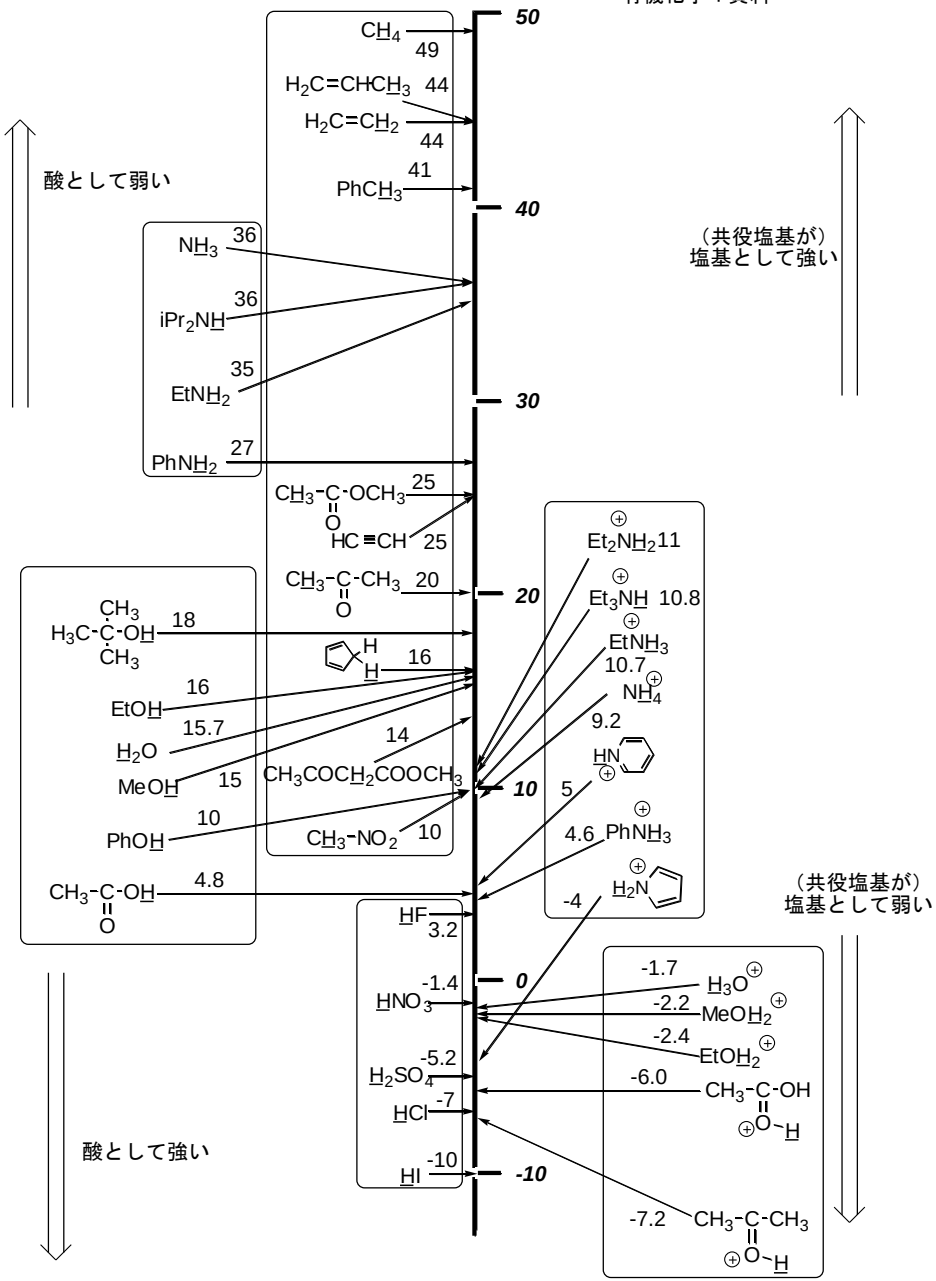
アンモニアのHOMO



水のHOMO



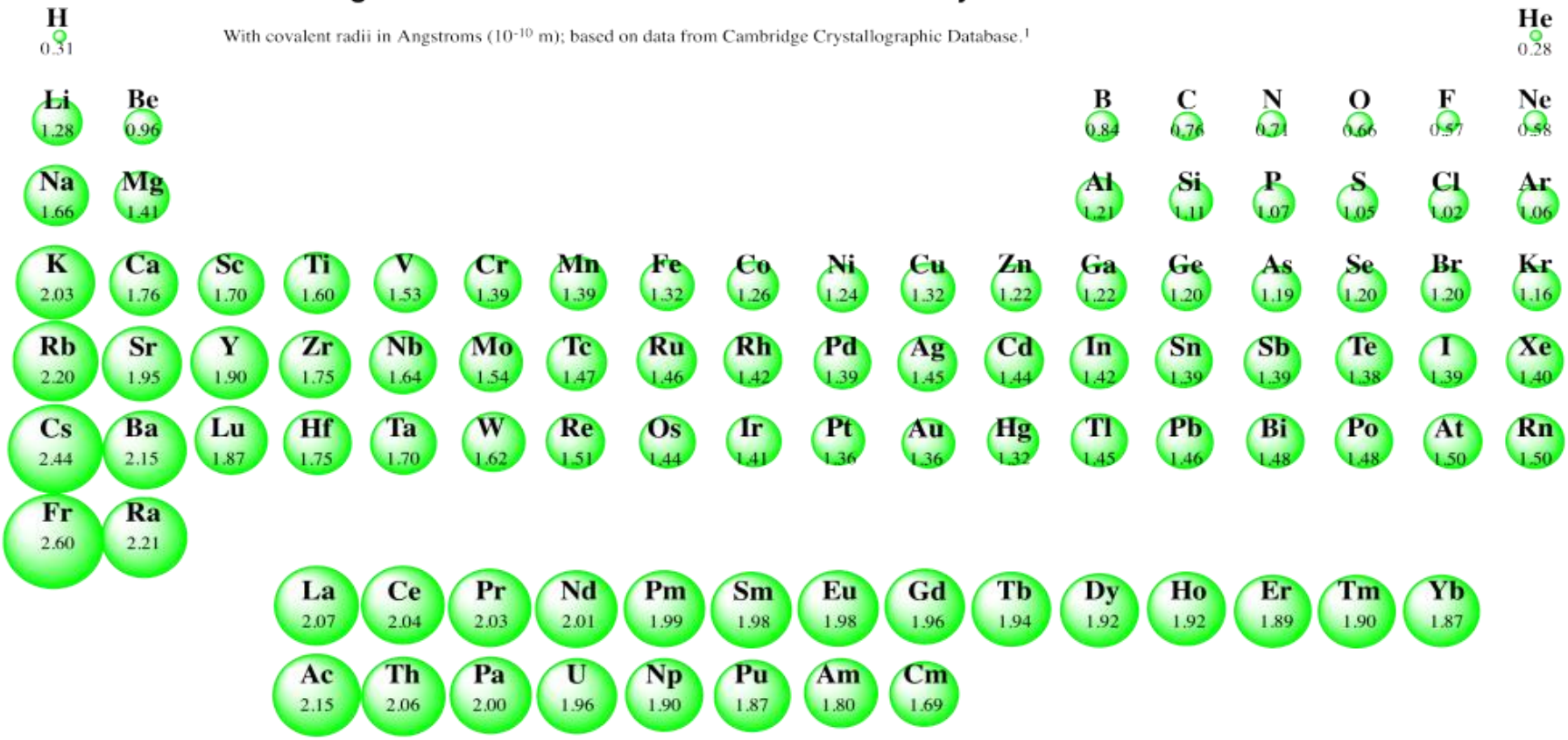
水中での値に換算したpKa値



Periodic Table of the Elements

College of Saint Benedict / Saint John's University

With covalent radii in Angstroms (10^{-10} m); based on data from Cambridge Crystallographic Database.[1]



1. Beatriz Cordero et al. *Dalton Trans.* **2008**, *21*,:2832–2838.

http://employees.csbsju.edu/cschaller/principles%20chem/appendix/appendix%20periodic%20radii.htm