Project 1 – Report

File: Chem4PB3_project_1_2017-solutions last changed: 02-Feb-2017

1. Formaldehyde – comparison of results from different methods Yellow shaded boxes are closest to experimental

Method ➔ Property ↓	#e-	AM1	MM - UFF	HF – STO-3G	HF STO-3G – forced C_{2v}	RHF 6311G forced C_{2v}	DFT B3LYP forced C_{2v}	Experimental E (eV), r (pm) wavenumbers
method		**AM1**	**UFF**	**RHF**	**RHF**	**RHF**	**DFT - B3LYP**	-
Basis set		**minimal**	**none**	**STO-3G**	**STO-3G**	**6-311G**	**6-311G**	-
# basis functions		10	-	12	12	32	32	-
# iterations		7	-		9 + 8+8+1	11+10+9+8+1	12+11+11+7+1	-
CPU time (s)		0.8	-	1.1	1.2	1.4	3.1	-
Energy (hartree)		0.0050243 (*)	0.00155839	-112.2920	-112.35435	-113.83952	-114.495835	-112.97
Dipole Moment (debye)		2.317	-	1.537	1.5366	2.9956	2.518	2.330
Reported symmetry		Cs	Cs	Cs	**C2v**	**C2v**	**C2v**	**C2v**
R(C=O) (pm)		122.73	122.73	1.2146	121.65	120.76	122.88	120.5
R(C-H) (pm)		111.05	111.05	109.72	110.11	11.8.18	119.96	111.1
ϕ(H-C=O) $(^o)$		122.22	120.0	122.3	122.75	121.63	121.90	121.9
ϕ(H-C-H) $(^o)$		115.55	120.0	114.2	114.51	116.74	116.2	116.13
Torsion (planarity) $(^o)$		179.998	179.998	179.998	180	180	180	180
1. O 1s – a1	2	-	-	552.51	552.51	559.93	520.89	539.48
2. C 1s – a1	2	-	-	302.60	302.60	308.72	279.69	294.47
3. O 2s – a1	2	39.05	-	36.38	36.38	38.85	29.36	24.60
4. C 2s – a1	2	25.05	-	21.97	21.97	23.90	17.64	23.00
5. σ(C-H) – b2	2	17.13	-	17.21	17.22	19.30	13.87	16.78
6. σ(C-H) – a1	2	16.25	-	14.84	14.84	17.57	12.24	16.00
7. π(C=O) – b2	2	14.54	-	12.06	12.06	14.52	11.02	14.38
8. O LP/CH – b1	2	10.78	-	9.64	9.64	12.08	7.52	10.88
9. π^*(C=O) - b2	0	-0.79		7.67	-7.67	-3.23	1.71	-
10. σ^*(C-H)	0	-3.17		17.09	-17.09	-4.26	-1.27	-
11. σ^*(C-H)	0	-4.00		19.96	-19.96	-5.66	-2.76	-
12. σ^*(C=O)	0	-6.06		24.84	-24.84	-8.83	-4.82	-
CH2 – s-str a1		3084	-	3643	3648	3259	3006	2783 (IR, R)
CO str a1		2053	-	2101	2101	1896	1732	1746 (IR)
CH2 scis a1		1442	-	1768	1767	1670	1554	1500 (IR, R)
CH2 a-str b1		3120	-	3496	3500	3169	2932	2843 (IR)
CH2 rock b1		1175	-	1398	1397	1378	1283	1249 (IR)
CH2 wag b2		1164	-	1280	1278	1337	1214	1167 (IR

Formaldehyde ground state

DETAILS of the calculations

AM1 – ZDO basis set **(*)** – computes valence electrons only
Geometry : Cs
E -0.05024 hartree (1 hartree = 27.2114 eV)
Imaginary freq: 0
Dipole moment: 2.3175

Molecular Mechanics – used UFF force field – Amber did not produce results
No electronic structure information, only geometry & Thermochemistry

HF- small basis set: restricted, STO-3G basis
Found I only ran it with frequency, not optimization
Re-ran using CLEAN, and POINT GROUP = C2v.
Did not run

```
-------------------------
 formaldehyde - HFR STO-3G
 -------------------------
 Redundant internal coordinates taken from checkpoint file:
 formaldehyde-HFR-STO-3G.chk
 Charge =  0 Multiplicity = 1
 C,0,0.0003993993,0.5337092874,0.
 O,0,-0.0002855611,-0.682808173,0.
 H,0,0.0006420806,1.1301760028,0.9262376467
 H,0,0.0006420806,1.1301760028,-0.9262376467
  WANTED AN INTEGER AS INPUT.
  FOUND A STRING AS INPUT.
 formaldehyde - HFR STO-3G
```

STRANGE - the com file looked sensible - could not see a non-numerical value
Problem was the additional keywords I had included, genchk in particular (*that allows restart but only works AFTER you have one valid calculation to generate the first *.chk*)

HF large basis set (6-311G)

There are now way more (8 occ, 24 unocc) basis functions than the minimal basis description used to generate the simple LCAO-MO picture. The (extra) unoccupied orbitals are usually viewed as ‘meaningless’ by the ab initio QM community. For spectroscopists however, they can be useful to describe the Rydberg excited states. In general they are ‘fluffier’ orbitals than those that come out of the STO-3G ‘minimal basis’ description. You need to look at the MO pictures to map specific ones of the 24 unocc. MOs in the 6311G picture to the 4 unocc. MOs of the minimal basis description.

```
Orbital symmetries:
       Occupied  (A1) (A1) (A1) (A1) (B2) (A1) (B1) (B2)
       Virtual   (B1) (A1) (B2) (A1) (A1) (B1) (B2) (B2) (A1) (A1)
                 (A1) (B1) (B2) (A1) (A1) (B2) (B1) (A1) (B2) (B1)
                 (B2) (A1) (A1) (A1)
 The electronic state is 1-A1.
 Alpha  occ. eigenvalues --  -20.58579 -11.34988  -1.42823  -0.87861  -0.70963
 Alpha  occ. eigenvalues --   -0.64584  -0.53386  -0.44419
 Alpha virt. eigenvalues --    0.11884   0.15668   0.20800   0.32454   0.47761
 Alpha virt. eigenvalues --    0.56668   0.56866   0.74066   0.81516   0.88062
 Alpha virt. eigenvalues --    1.05700   1.10062   1.18160   1.62445   2.44763
 Alpha virt. eigenvalues --    2.52449   2.91937   3.18308   3.25682   5.34591
 Alpha virt. eigenvalues --    5.40918   5.45663  24.43323  51.47363
```

Some general comments

1. **AM1 is by FAR the best at computing orbital energies that agree with PES IPs**, within Koopman’s Theorem. Perhaps that is no surprise as AM1 is most likely parametrized based on matching to valence IPs as well as other data. See http://openmopac.net/manual/semiempirical_theory.html for details on how the parameters in various semi-empirical codes were established.

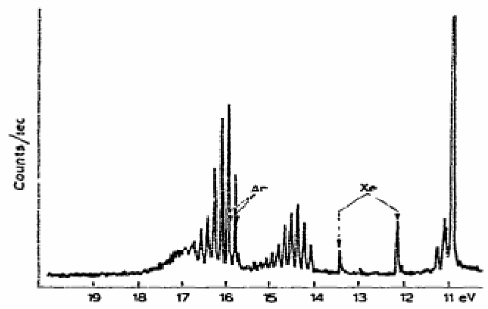
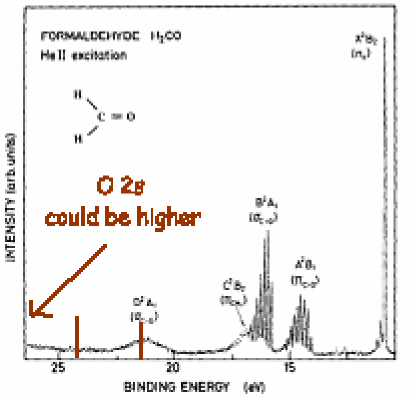
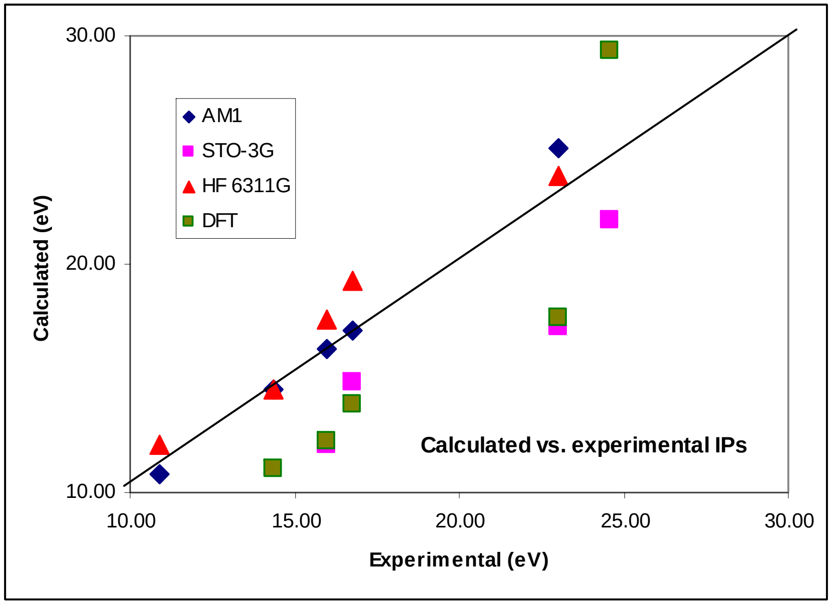
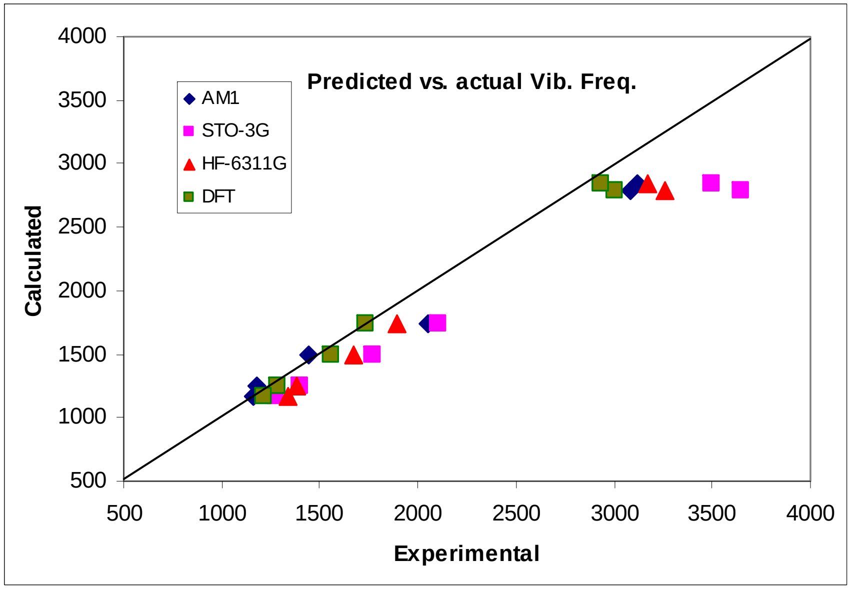


Fig. 10. Helium 584 Å photoelectron spectrum of formaldehyde.







Experimental data

source of GEOMETRY, dipole moment: http://cccbdb.nist.gov/exp2.asp?casno=50000

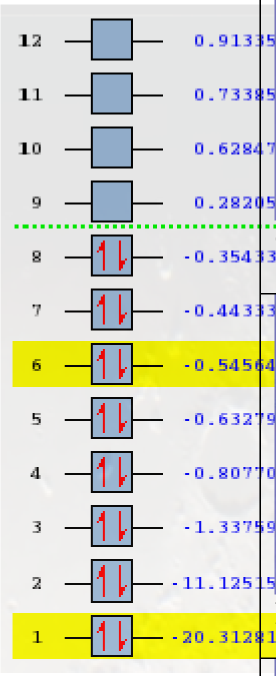
Sources of photoelectron spectra & IPs

(a) **XPS** K. Kuramoto, M. Ehara, H. Nakatsujia, M. Kitajima, H. Tanaka, A. De Fanis, Y. Tamenori, K. Ueda
J. El. Spec 142 (2005) 253–259

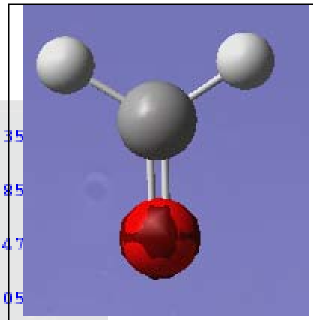
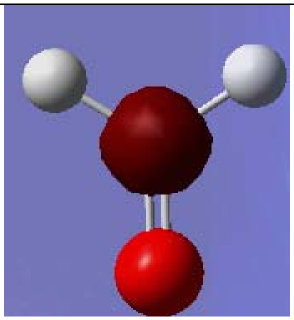
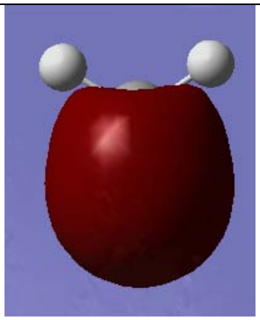
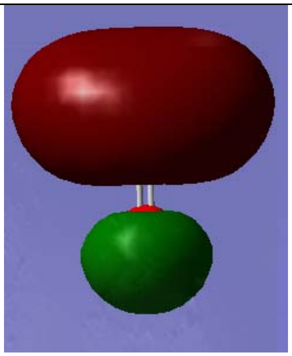
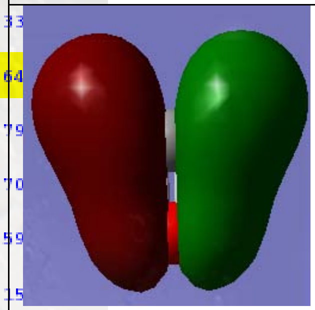
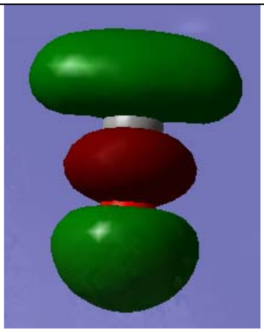
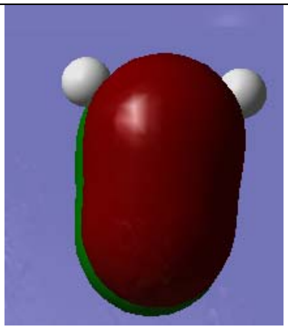
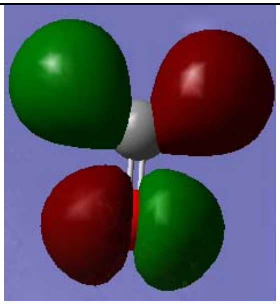
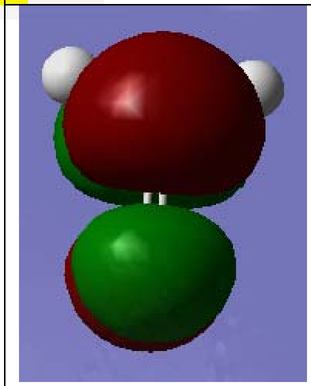
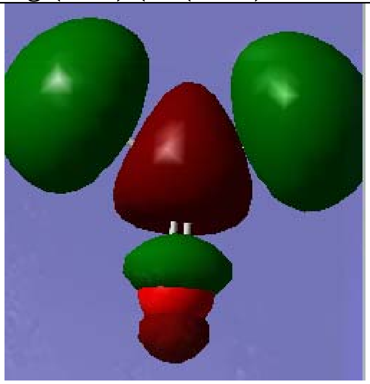
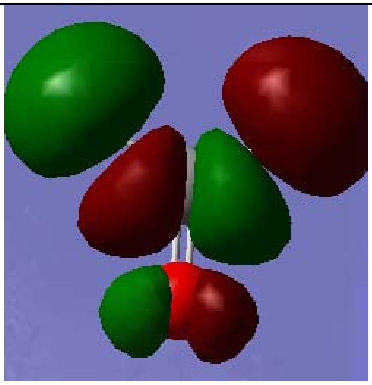
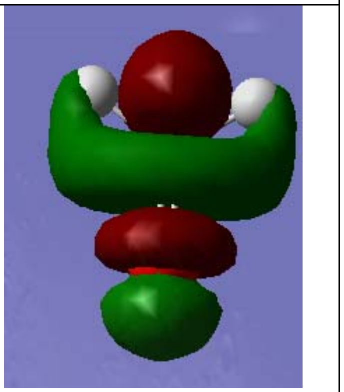
(b) PES He(II) M.P. Kean, S. Lunell, A. Naves de Brito, M. Carlsson-Gothea, S. Svensson, B. Wannberg and L. Karlsson, J. El. Spec 56 (1991) 313-339

(c) PES He(I) - A. D. Baker, C. Barer, C.R. Brundle and D. W. Turner,, Int. J. Mass Spec 1 (1968) 285
Adiabatic 10.88(4) eV, 14.09(5) eV, 15.85(4) eV, and 16.25(4) eV , ~20.5
Vertical 10.88(4) eV, 14.38(8)eV, 16.00(9)eV, and 16.78 eV

Orbital plots
(HF STO-3G)



using the default
e- threshold

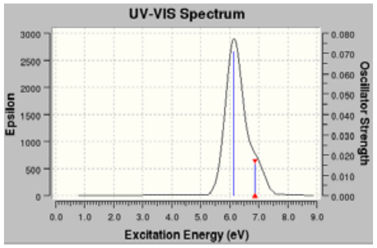
 O 1s a1	 C 1s a1	 O 2s a1	 C 2s a1
 Pi & C-H	 sig (C-H) (σ*(C=O)	 π(C=O)	 σ(C-H) (& O lone pair
 π*(C=O)	 σ*(C-H)	 σ*(C-H)	 σ*(C=O)

1b. Electronic (UV-vis) Spectroscopy (Ann. Rev. Phys. Chem. 1983. 34: 31-58)

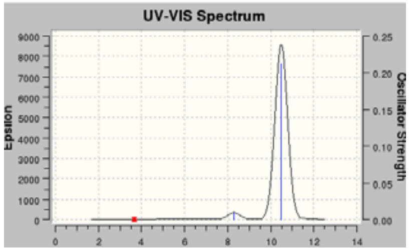
For the HF (STO-3G), HF (6-311G) and DFT calculations, **using the TDSCF energy method g**ives

Excited state		AM-1	HF-STO-3G	HF-6-311G	DFT BL3LYP	EXPERIMENT
1	symmetry	A2	A2	A2	A2	
	Energy (eV)	**2.779**	**3.668**	**3.829**	**3.856**	**3.94**
	Intensity (osc str)	0	0	0	0	
	Dominant config	6 ➔ 7 (0.705) NB add 2 to match orb#	5 -> 9 (.12) 8 -> 9 (.70)	8 -> 9 (0.70)	8 -> 9 (0.70)	
2	symmetry	B1	B1	B1	B1	
	Energy (eV)	**6.143**	**8.30**	**8.31**	**8.95**	**8.11**
	Intensity (osc str)	0.071	0.0092	0.0021	0.0051	
	Dominant config	6 -> 8 (.61)	6 -> 9 (.71)	6 -> 9 (.70)	6 -> 9 (.70)	
3	symmetry	A1	A1	B2	B2	
	Energy (eV)	**6.878**	**10.49**	**10.43**	**9.154**	**8.37**
	Intensity (osc str)	0.017	0.212	0.113	0.165	
	Dominant config	6 -> 9 (0.62)	6 -> 12 (.18) 7 -> 9 (.68)	8 -> 10 (0.69)	8 -> 10 (0.71)	

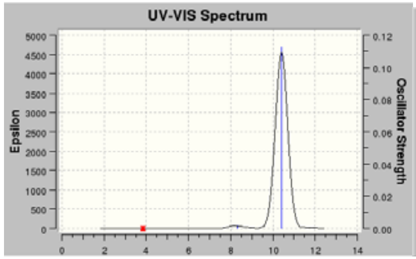
AM-1



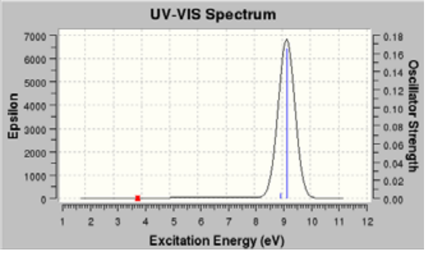
HF STO-3G E in eV



HF 6-311G



DFT BL3LyP 6-311G



STO-3G output

Excited State 1: **Singlet-A2** 3.6681 eV 338.01 nm **f=0.0000** <S**2>=0.000

5 -> 9 0.12479

8 -> 9 0.69907 **Homo (O LP) ➔ Lumo ($\pi^*_{C=O}$) A_1 ➔ A_2 forbidden in C_{2v}**

Excited State 2: **Singlet-B1** 8.3005 eV 149.37 nm **f=0.0092** <S**2>=0.000

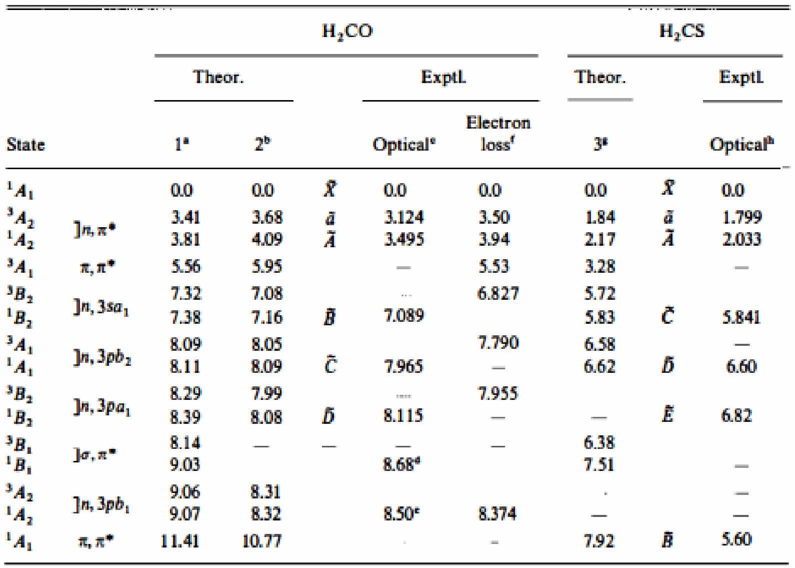
6 -> 9 0.70825 **σ(C-H) – a1 ➔ Lumo (π*)**

Excited State 3: **Singlet-A1** 10.4891 eV 118.20 nm **f=0.2124** <S**2>=0.000

6 -> 12 0.17930 7 -> 9 0.68392 **$\pi_{C=O}$ – a1 ➔ Lumo (π*)**

Formaldehyde is a common preservative in cosmetics, but this compound is also known as an irritant agent that can cause contact allergy [1]. Formaldehyde is frequently used in water-based formulations such as shampoo, conditioner, shower/bath gel, liquid hand wash. [2]. Even products designed for children such as bubble bath or baby shampoo include formaldehyde in their composition. (Analytica Chimica Acta 674 (2010) 59–63)

Table 13 Comparison of calculated vertical excitation energies for H_2CO and H_2CS (in eV) with experimental data



		H_2CO					H_2CS		
		Theor.			Exptl.		Theor.		Exptl.
State		1^a	2^b		Optical^c	Electron loss^f	3^g		Optical^h
$^1A_1$		0.0	0.0	$\tilde{X}$	0.0	0.0	0.0	$\tilde{X}$	0.0
$^3A_2$	$]n, \pi^*$	3.41	3.68	$\tilde{a}$	3.124	3.50	1.84	$\tilde{a}$	1.799
$^1A_2$		3.81	4.09	$\tilde{A}$	3.495	3.94	2.17	$\tilde{A}$	2.033
$^3A_1$	π, π^*	5.56	5.95		—	5.53	3.28		—
$^3B_2$	$]n, 3sa_1$	7.32	7.08		···	6.827	5.72		
$^1B_2$		7.38	7.16	$\tilde{B}$	7.089		5.83	$\tilde{C}$	5.841
$^3A_1$	$]n, 3pb_2$	8.09	8.05			7.790	6.58		—
$^1A_1$		8.11	8.09	$\tilde{C}$	7.965	—	6.62	$\tilde{D}$	6.60
$^3B_2$	$]n, 3pa_1$	8.29	7.99		····	7.955			
$^1B_2$		8.39	8.08	$\tilde{D}$	8.115	—	—	$\tilde{E}$	6.82
$^3B_1$	$]\sigma, \pi^*$	8.14	—	—	—	—	6.38		
$^1B_1$		9.03			8.68^d		7.51		—
$^3A_2$	$]n, 3pb_1$	9.06	8.31				·		—
$^1A_2$		9.07	8.32		8.50^e	8.374	—		—
$^1A_1$	π, π^*	11.41	10.77		·	-	7.92	$\tilde{B}$	5.60

[a] Ref. (75).
[b] Ref. (77).
[c] The values refer to the 0-0 bands, see Tables 9 and 11 and Ref. (78).
[d] Ref. (79).
[e] Assigned as the $6^1{}_0$ band.
[f] The values refer to vertical excitation energies, Ref. (66).
[g] Ref. (47).
[h] The values refer to 0-0 bands, see Tables 9 and 11 and Refs. (80–82).

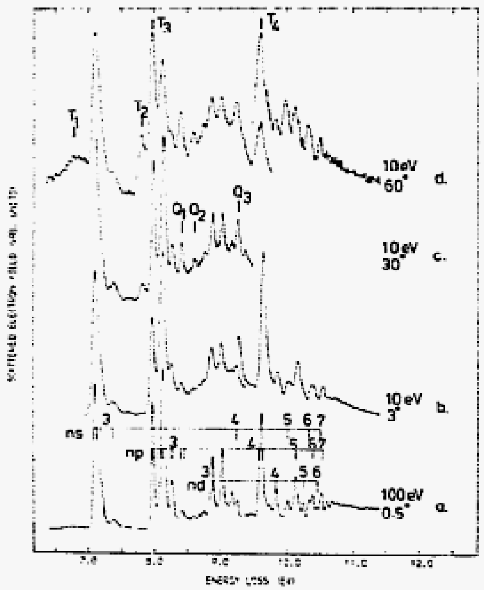


Fig. 3. Energy-loss spectra of CH_2O showing Rydberg series converging on the first ionization limit. The scattering angle and electron energies used are shown against each spectrum. Three optically observed series [2] are indicated on spectrum (a). The peaks marked T_1 to T_4 and Q_1 to Q_3 are believed to be spin forbidden, and electric quadrupole allowed transitions respectively.

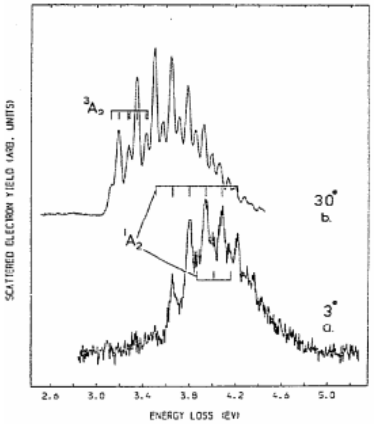
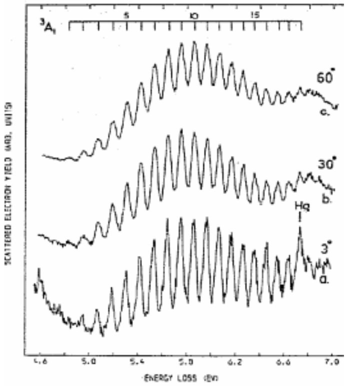


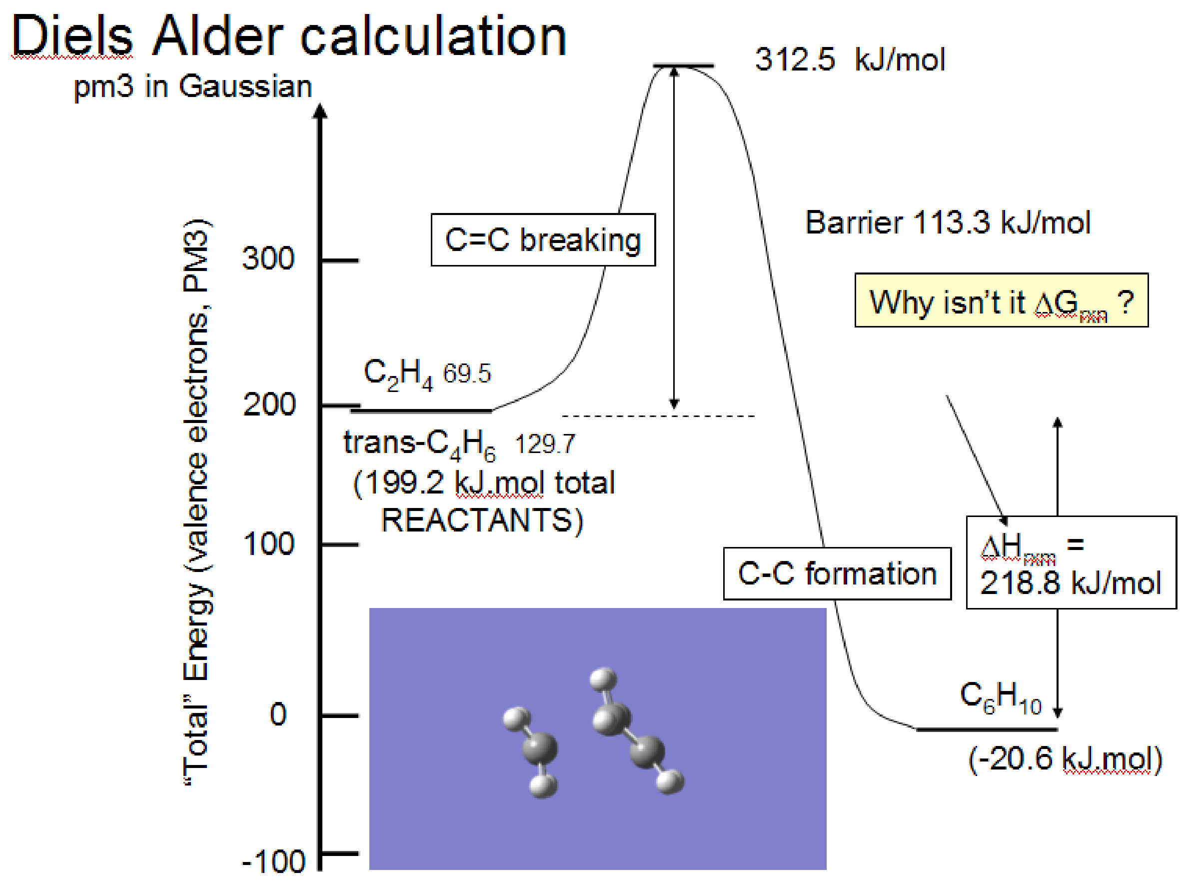
Fig. 1. Energy-loss spectra of formaldehyde vapour covering the range 2.6–5.2 eV at a residual energy of 10 eV and scattering angles of 3 and 30°. The assignments indicated are taken from ref. [8].



ig. 2. Energy-loss spectra of CH_2O covering the range 4.6–7.0 eV at a residual energy of 10 eV. The feature marked "Hg" is believed to be an atomic mercury transition arising rom the mercury diffusion pump used to evacuate the spec-rometer

2. **Diels-Alder reaction** – PM3 semiempirical calculation
Ground state Energies 1 atomic unit (or Hartree) equals 2625.5 kJ/mol

	pm3		HF 3-21G
Molecule	Total energy (Hartree)	Total energy (kJ/mol)	Total E (10^5 kJ/mol)
1,3-Butadiene - cis	0.0505507	132.7	-
1,3-Butadiene - trans	0.0493885	129.7	-4.005
Ethene	0.0264660	69.5	-2.018
REACTANTS		199.2	-6.023
Cyclohexene	-0.0078478	-20.6	-6.025
Transition state	0.119012	312.5	-6.022



Cis-Butadiene – followed the instructions in the Harvey website

NB the starting geometry was not carefully done. Perhaps should do an MM optimization first ?
(Spartan had a ‘clean-up’ procedure in its input process; Gaussian has the same – Edit~Clean)

For butadiene – there are multiple “SCF done” cycles – have to get to the LAST ONE to get final optimized energy

```
line 248/4645       SCF Done:  E(RPM3) =  0.970178385728     A.U. after   20 cycles
line 479/4645       SCF Done:  E(RPM3) =  0.890625711311     A.U. after   16 cycles
line 652/4645       SCF Done:  E(RPM3) =  0.746143927805     A.U. after   16 cycles
line 826/4645       SCF Done:  E(RPM3) =  0.493109134248     A.U. after   14 cycles
line 998/4645       SCF Done:  E(RPM3) =  0.230827211676     A.U. after   13 cycles
line 1172/4645      SCF Done:  E(RPM3) =  0.147369903695     A.U. after   12 cycles          geometry restored to original
line 1343/4645      SCF Done:  E(RPM3) =  0.901137937061E-01 A.U. after   12 cycles
. . . .
line 4371/4645      SCF Done:  E(RPM3) =  0.505509506176E-01 A.U. after   13 cycles
```

============ used clean , and then the default input file, not the Harvey modified one

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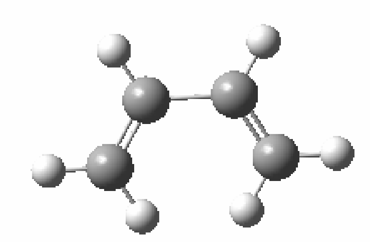
line 248/1774   SCF Done:  E(RPM3) =  0.601296417956E-01 A.U. after   12 cycles
. . .
line 1503/1774  SCF Done:  E(RPM3) =  0.505507341102E-01 A.U. after   13 cycles
```

============ using the Harvey format, get same answer

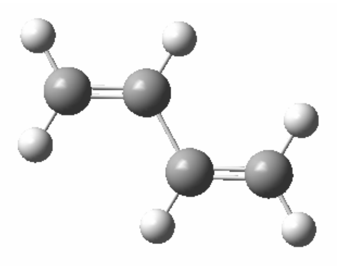
```
line 1503/1774  SCF Done:  E(RPM3) =  0.505507341102E-01 A.U. after   13 cycles
```

========================

Cis-Butadiene



Trans butadiene



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Trans butadiene
line 993/1278 SCF Done: E(RPM3) = 0.493884530507E-01 A.U. after   13 cycles

Energy difference (cis – trans) = 3.05 kJ/mol
http://chemistry.umeche.maine.edu/Modeling/donmolmech.html
[literature says trans is more stable than cis by 3.21 kcal/mol, or **0.77 kJ/mol**]
Thus pm3 method over-estimates the Thermochemistry by ~*4

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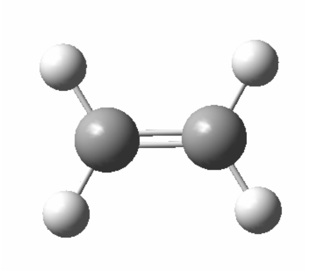
Ethene
SCF Done: E(RPM3) = 0.264660251344E-01 A.U. after   7 cycles



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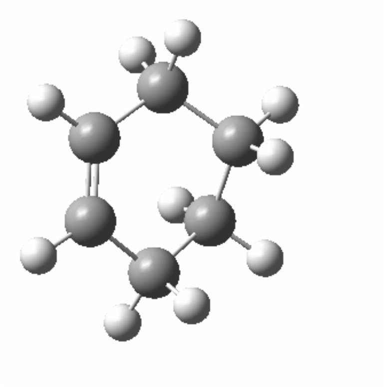
Cyclohexene

SCF Done: E(RPM3) = -0.784776827086E-02



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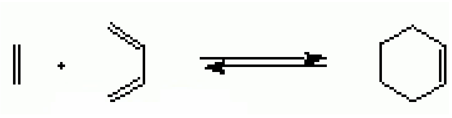
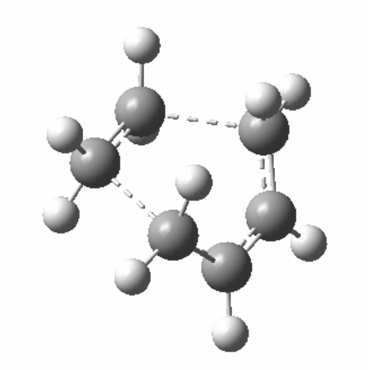
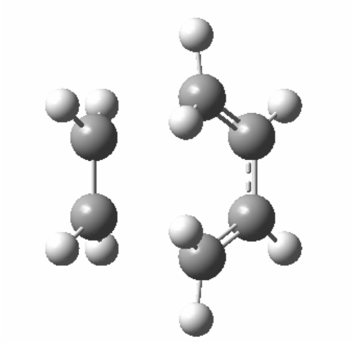
Diels Alder Thermochemistry





=============➔



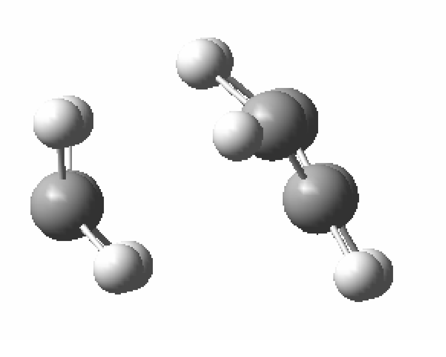
using the supplied ‘hint’ geometry, but had to rebond in a sensible manner

1st try, I used just OPT & TS (Berny) ➔ structure reverted to two non-bonded molecules with delocalized bonding in the butadiene

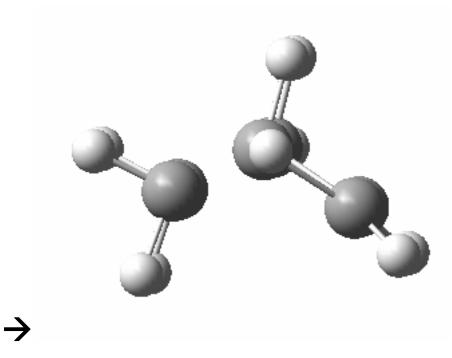
2nd try, I added partial bonds to make the D-A adduct, and then used OPT&FREQ

line 3212/4218 SCF Done: E(RPM3) = 0.119012226305 A.U. after 2 cycles is LAST of the SCF Done

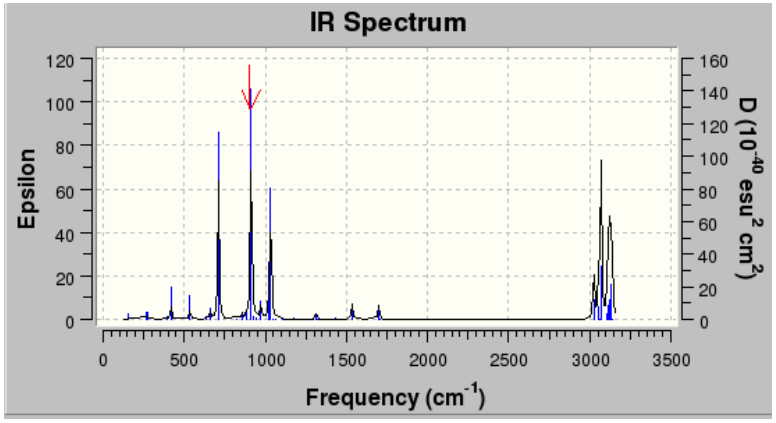
imaginary frequency (the ethane moving against the cis butadiene) = **- 934 cm^{-1}**



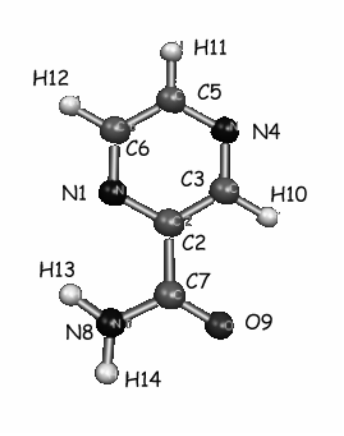
↔



Movie made of the motion along the reaction co-ordinate (the imaginary frequency)



3. nmr calculation for pyrazinamide – used RHF/6-31G calculations (forgot the ‘d’)



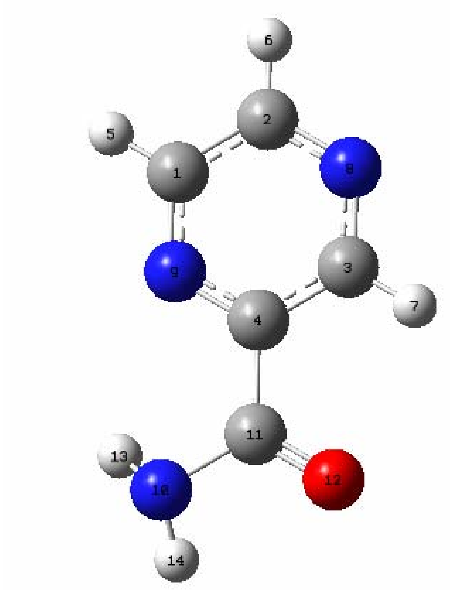
from my RHF/6-31G calc

nucleus	Chem. Shift	ppm wrt ref.	Calc (*)	isotropic	anisotropy
C2	**146.4**	**146.56**	138.3	53.4	157.9
C3	**145.0**	**148.74**	140.7	51.2	185.2
C5	**144.4**	**149.52**	140.8	58.3	167.0
C6	**148.2**	**141.66**	135.4	-56.6	180.2
C7	**165.1**	**193.96**	151.6	6.02	145.1
H10	**9.2**	**10.11**	9.6	22.5	7.7
H11	**8.7**	**9.19**	8.6	23.4	5.5
H12	**8.5**	**8.80**	8.3	23.8	5.4
H13	**7.9**	**4.56**	6.7	28.0	8.3
H14	**8.3**	**3.91**	4.0	28.7	10.0

(*) Chis et al. Chem. Phys 316 (2005) 153 ; B3LYP/6-31G(d) for C-1 monomer (see below)

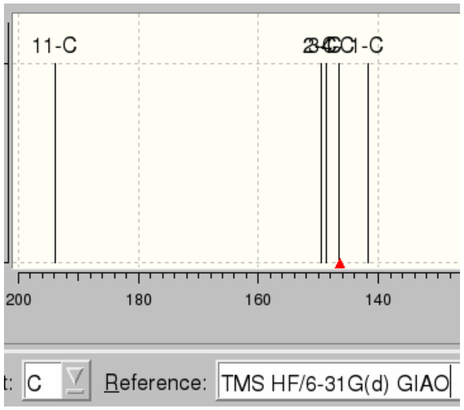
My geometry

1	C5	1.69854	-0.8603	-0.88031
2	C6	2.3521	0.35154	-0.61911
3	C3	0.32748	1.31902	-0.04187
4	C2	-0.32608	0.10718	-0.30307
5	H12	2.25876	-1.70987	-1.2109
6	H11	3.41133	0.42723	-0.75026
7	H10	-0.23274	2.16859	0.28871
8	N4	1.65172	1.41366	-0.20582
9	N1	0.3743	-0.95494	-0.71635
10	N8	-2.53614	-1.27292	-0.3883
11	C7	-1.85058	-0.00176	-0.11431
12	O	-2.50945	0.99739	0.27448
13	H13	-1.91325	-2.03366	-0.20584
14	H14	-3.3402	-1.35177	0.201



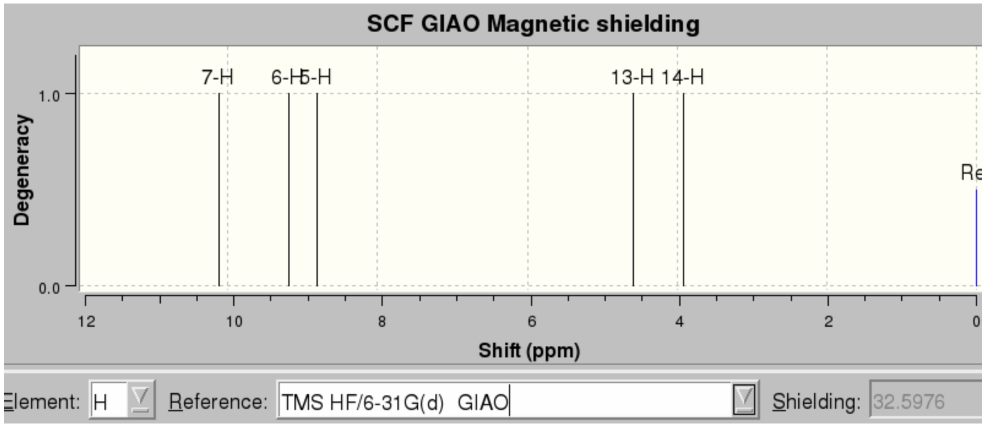
C nmr

H nmr



t: C

Reference: TMS HF/6-31G(d) GIAO



Element: H

Reference: TMS HF/6-31G(d) GIAO

Shielding: 32.5976

The poor agreement of the predicted ^{1}H chemical shifts for H13 and H14 with experiment are because **this molecule likes to dimerize by forming H-bonds between H14-O9** (see V. Chis et al. Chemical Phys. 316 (2005) 153). Note that the Chis et al calculations also show **BOTH H-13 and H-14 too low**, even though <u>only H-14 is implicated in the H-bonding</u>.

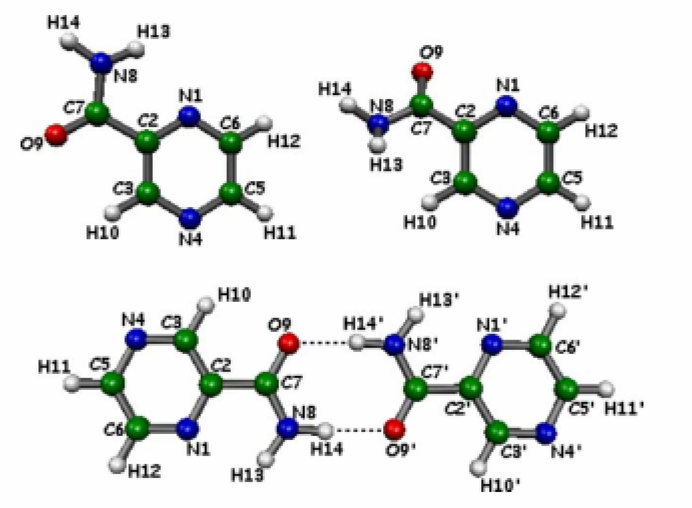
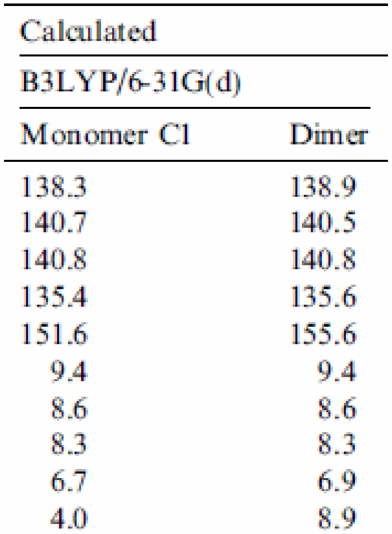


Fig. 1. Molecular structure and atom numbering scheme for the two conformers of pyrazinamide (C1 – top left, C2 – top right) and pyrazinamide dimer (bottom).



Calculated	
B3LYP/6-31G(d)	
Monomer C1	Dimer
138.3	138.9
140.7	140.5
140.8	140.8
135.4	135.6
151.6	155.6
9.4	9.4
8.6	8.6
8.3	8.3
6.7	6.9
4.0	8.9