

Project 1 – Report

File: Chem4PB3_project_1_2019-solutions last changed: 29 Jan 2019

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

Property ↓	Method →	#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) (°)			122.22	120.0	122.3	122.75	121.63	121.90	121.9
φ(H-C-H) (°)			115.55	120.0	114.2	114.51	116.74	116.2	116.13
Torsion (planarity) (°)			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

Geometry : Cs

E -0.05024 hartree (1 hartree = 27.2114 eV)

Imaginary freq: 0

Dipole moment: 2.3175

(*) – computes valence electrons only

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.

Initially it 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
```

of iterations

In most of the calculations you need to look through the log files in some detail, since there are multiple steps of SCF as the geometry is optimized, so the answer required is the SUM of those steps.

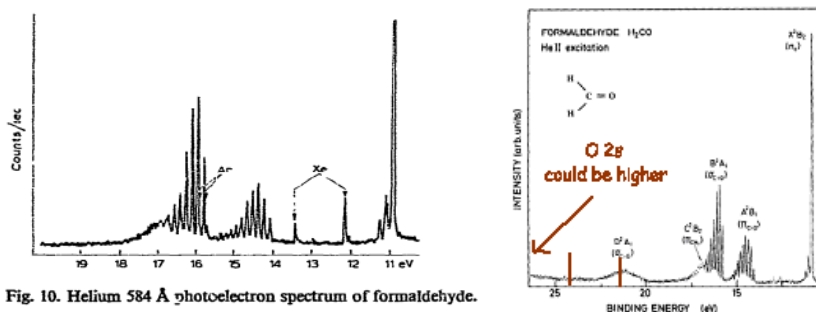
DFT with B3LYP functional and 6-311G basis set

The project statement stated : “use B3LYP functional and the default basis set Gaussian suggests. This is 3-21G when starting from a clean version of GV without predefined structure. In fact, it is probably better to improve the flexibility of the basis set, since DFT is generally better than a solely HF calculation. I chose to use the 6-311G basis.

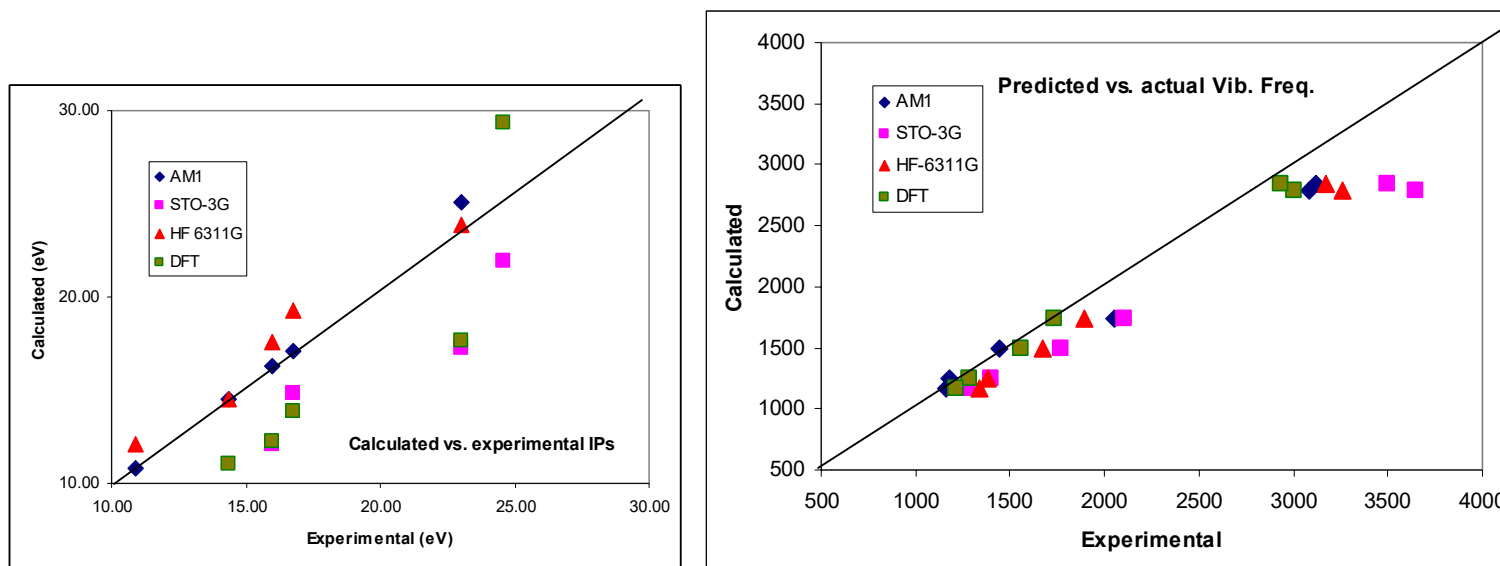


Some general comments

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. AM1 also gave the best value of the dipole moment, which is usually a sensitive probe of how well a calculation is reproducing the total electron density. No one method excelled at the molecular geometry. Surprisingly Molecular Mechanics did NOT get best geometry (except C-H bond length), despite the fact it is usually used to set geometry (it is the basis of the 'clean' function in GassuView)..



2. The DFT calculation (B3LYP functional, 311G basis set) gave the best values of the vibrational frequencies



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

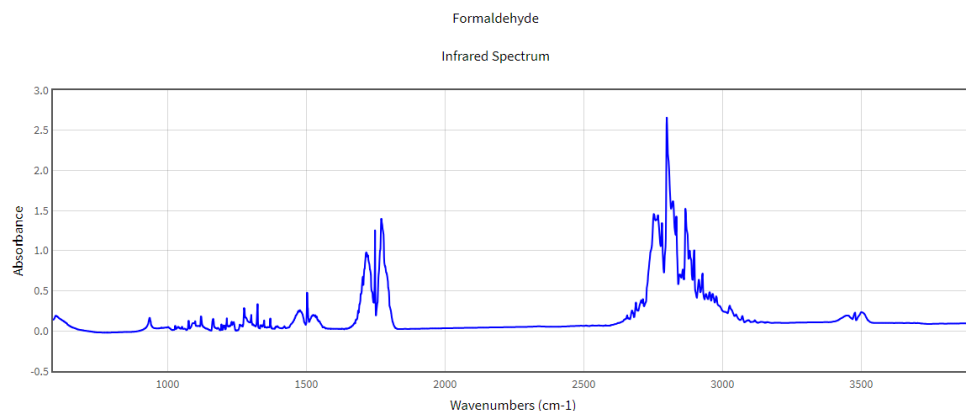
Adiabatic 10.88(4) eV, 14.09(5) eV, 15.85(4) eV, and 16.25(4) eV , ~20.5

Vertical 10.88(4) eV, 14.38(8)eV, 16.00(9)eV, and 16.78 eV

Source of vibrational frequencies

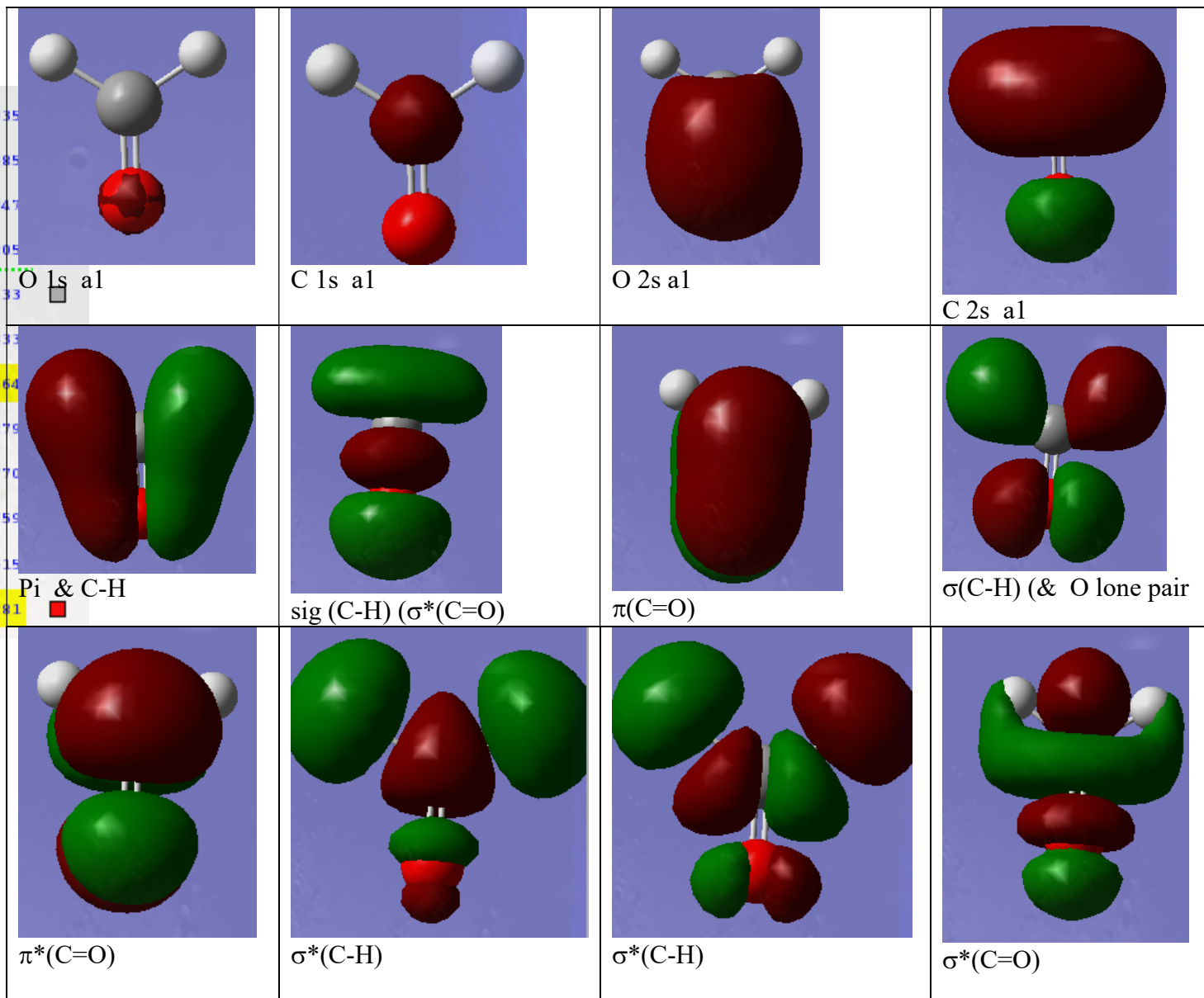
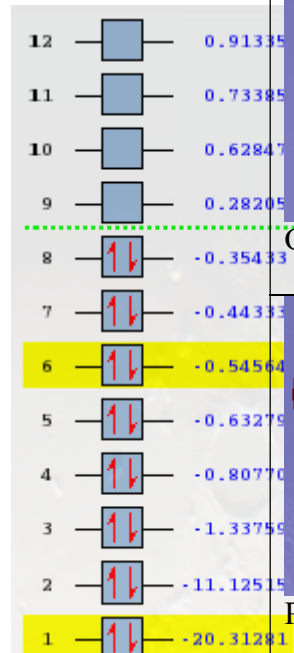
(a) D. J. Clouthier and D. A. Ramsay, The Spectroscopy of Formaldehyde And Thioformaldehyde Ann. Rev. Phys. Chem. 34 (1983) 31-58.

(b) <https://webbook.nist.gov/cgi/cbook.cgi?ID=50000&cIR=on> - gas phase IR spectrum of Formaldehyde



Sym. Species	No	Approximate type of mode	Selected Freq. Value	Rating	Infrared Value	Phas
a ₁	1	CH2 s-str	2783	A	2782.5	S gas
a ₁	2	CO str	1746	A	1746.1	V S gas
a ₁	3	CH2 scis	1500	A	1500.1	S gas
b ₁	4	CH2 a-str	2843	A	2843.1	V S gas
b ₁	5	CH2 rock	1249	A	1249.1	S gas
b ₂	6	CH2 wag	1167	A	1167.3	S gas

Orbital plots
(HF STO-3G)



using the default
e- threshold

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** gives

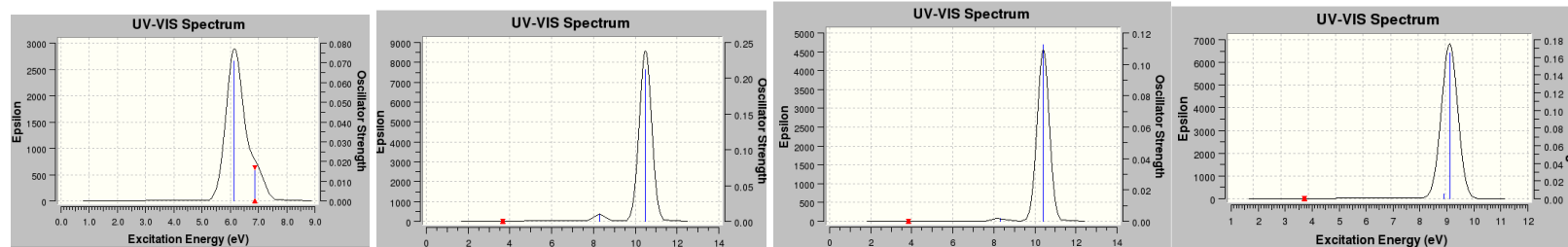
Excited state	AM-1	HF-STO-3G	HF-6-311G	DFT BL3LYP	EXPERIMENT
1	symmetry	A2	A2	A2	
	Energy (eV)	2.779	3.668	3.829	3.94
	Intensity (osc str)	0	0	0	
	Dominant config	6 → 7 (0.705) NB add 2 to match orb#	5 → 9 (.12) 8 → 9 (.70)	8 → 9 (0.70)	
2	symmetry	B1	B1	B1	
	Energy (eV)	6.143	8.30	8.31	8.11
	Intensity (osc str)	0.071	0.0092	0.0021	0.0051
	Dominant config	6 → 8 (.61)	6 → 9 (.71)	6 → 9 (.70)	
3	symmetry	A1	A1	B2	
	Energy (eV)	6.878	10.49	10.43	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 ($\pi^*_{C=O}$)**

$A_1 \rightarrow A_2$ transitions are 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 **$\sigma(C-H) - a1 \rightarrow LUMO (\pi^*)$**

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 **$\pi_{C=O} - a1 \rightarrow LUMO (\pi^*)$**

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 H₂CO : experimental data

State	H ₂ CO				
	Theor.		Exptl.		Electron loss ^f
	1 ^a	2 ^b	Optical ^e		
¹ A ₁	0.0	0.0	\bar{X}	0.0	0.0
³ A ₂	3.41	3.68	\bar{a}	3.124	3.50
¹ A ₂	3.81	4.09	\bar{A}	3.495	3.94
³ A ₁	5.56	5.95	—	—	5.53
³ B ₂	7.32	7.08	—	—	6.827
¹ B ₂	7.38	7.16	\bar{B}	7.089	—
³ A ₁	8.09	8.05	—	—	7.790
¹ A ₁	8.11	8.09	\bar{C}	7.965	—
³ B ₂	8.29	7.99	—	—	7.955
¹ B ₂	8.39	8.08	\bar{D}	8.115	—
³ B ₁	8.14	—	—	—	—
¹ B ₁	9.03	—	—	8.68 ^d	—
³ A ₂	9.06	8.31	—	—	—
¹ A ₂	9.07	8.32	—	8.50 ^e	8.374
¹ A ₁	11.41	10.77	—	—	—

^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 6¹₀ 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).

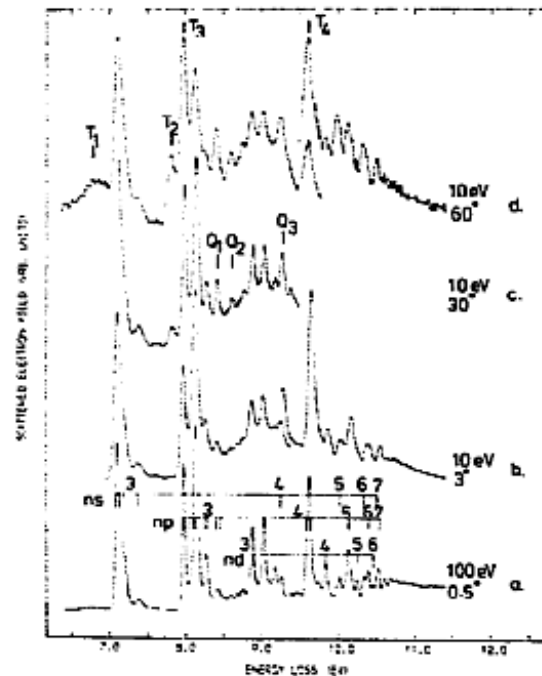


Fig. 3. Energy-loss spectra of CH₂O showing Rydberg series converging on the first ionization limit. The scattering angle and electron energies used are shown against each spectrum. Three optically observed series [2] are indicated on spectrum (a). The peaks marked T₁ to T₄ and Q₁ to Q₃ are believed to be spin forbidden, and electric quadrupole allowed transitions respectively.

The **OPTICALLY FORBIDDEN** X ¹A₁ → A ¹A₂ **electronic transition** CAN be seen using inelastic electron scattering, if low impact energy and finite scattering angle is used. As the angle increases, singlet → triplet transitions start to be observed

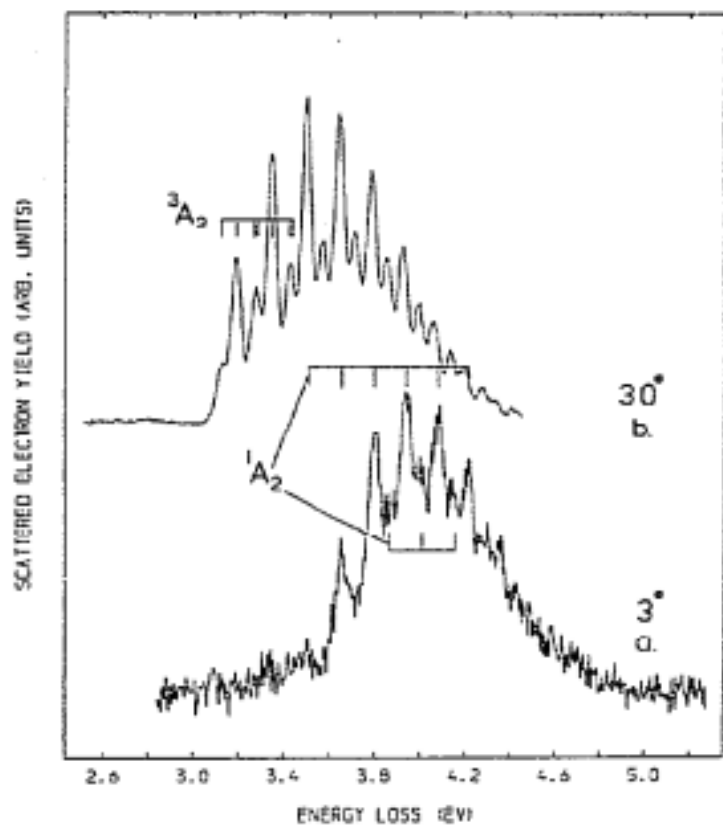


Fig. 1. Energy-loss spectra of formaldehyde vapour covering the range 2.6–5.2 eV at a residual energy of 10 eV and scattering angles of 3 and 30°. The assignments indicated are taken from ref. [8].

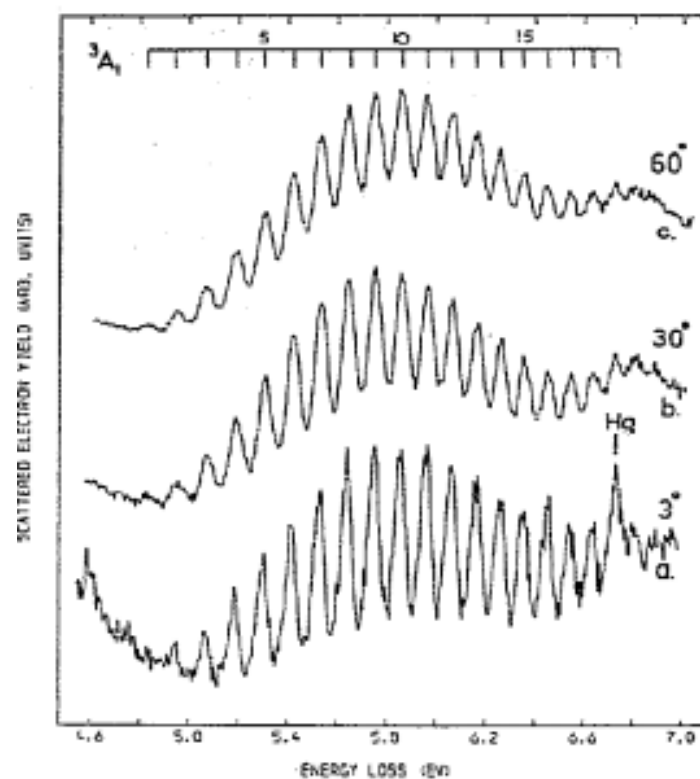


Fig. 2. Energy-loss spectra of CH₂O covering the range 4.6–7.0 eV at a residual energy of 10 eV. The feature marked "Hg" is believed to be an atomic mercury transition arising from the mercury diffusion pump used to evacuate the spectrometer.