

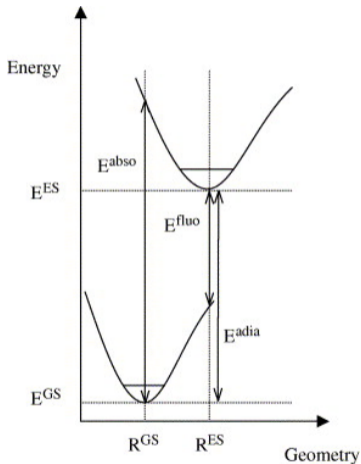


*Expertise from Knowledge*



## Absorbtion and emission spectra of formaldehyde

# Background



Fomaldehyde is the prototype molecule for studying the  $n \rightarrow \pi^*$  type of excitation chromophores. Here is a schematic presentation of the processes that we are going to study in this session.  $R^{GS}$  and  $R^{ES}$  represent the ground and excited state minimum geometries, respectively.  $E^{GS}$  and  $E^{ES}$  are the corresponding energies.  $E^{abso}$ ,  $E^{fluo}$  and  $E^{adia}$  are the absorption, fluorescence and adiabatic transition energies, respectively.

From <http://dx.doi.org/10.1016/j.cpllett.2006.01.068>

# Outline

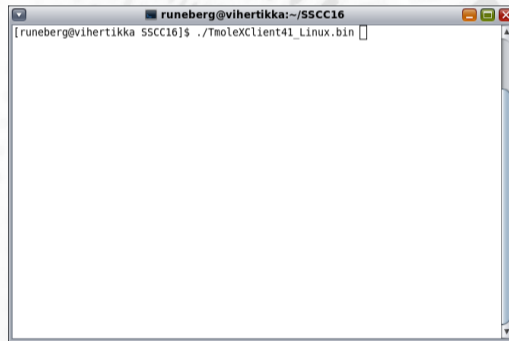
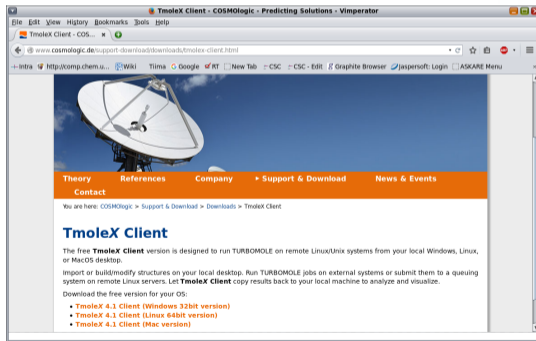
We are using Turbomole 7.1/TmoleX 4.2/TD-DFT to study formaldehyde in order to:

- ▶ Obtain the equilibrium structure of the ground state
- ▶ Calculate the vertical absorption spectrum of the ground state
- ▶ Identify and characterize the first excited state
- ▶ Optimize the structure of the first excited state
- ▶ Calculate the emission spectrum of the first excited state

# Download and install TmoleX

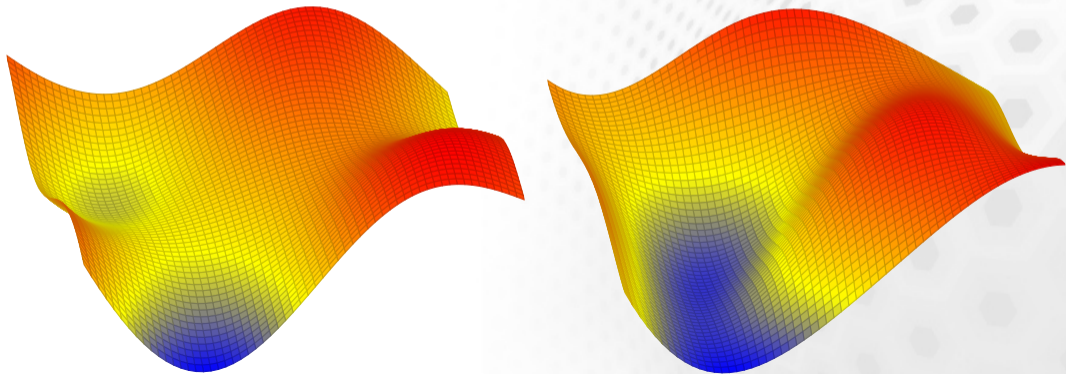
Download the TmoleX GUI client from

<http://www.cosmologic.de/support-download/downloads/tmolex-client.html>  
(Users who feel more comfortable working from the command line are of course free to do so)

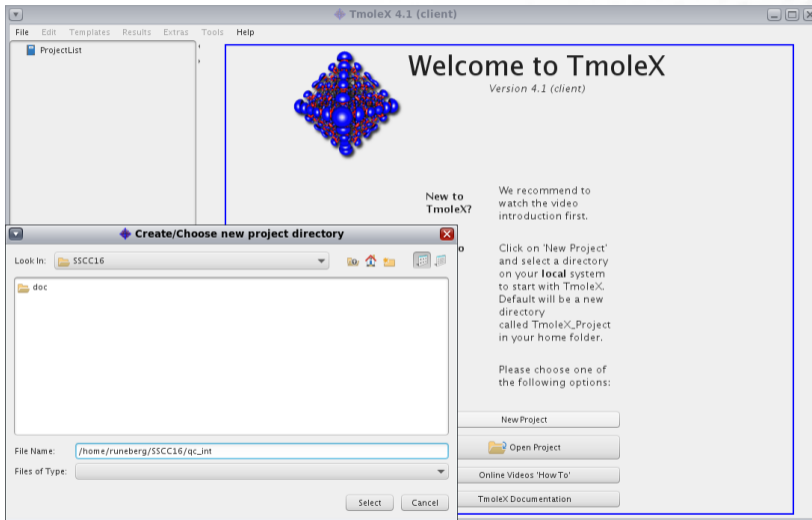


# Task 1: Optimize ground state structure of formaldehyde

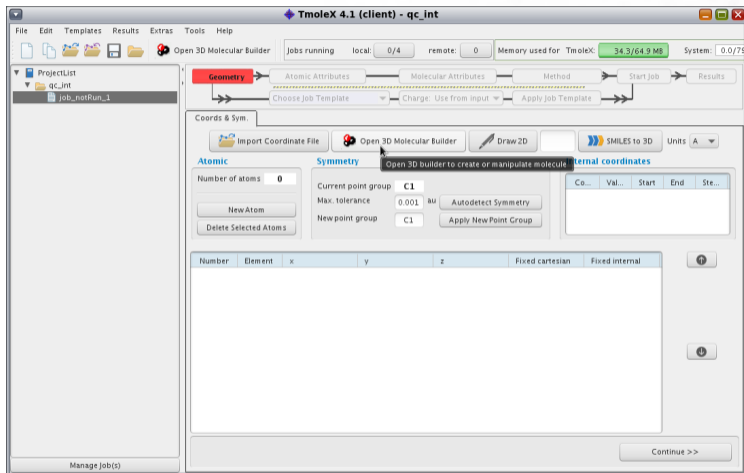
We need an initial guess for the geometry specifying the  $3N-6$  internal nuclear coordinates. This initial structure place the system on the energy surface that is uniquely defined by the computational model we are going to use (B-O approx.). The performance of the model often vary at different parts of the surface.



# Launch TmoleX and create a new project



# Define your first Turbomole job

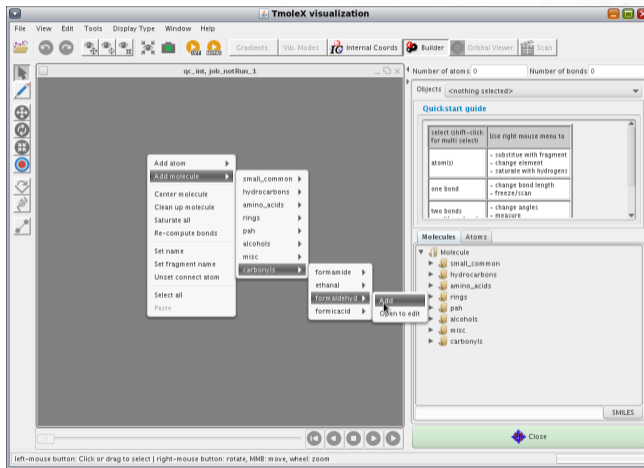


A complete Turbomole job comprises the sequence:

**Geometry - Atomic Attributes - Molecular Attributes - Method - Start Job - Results**

# Geometry: Build formaldehyde

Open the 3D builder, right-click on canvas and load formaldehyde from the library



Close the builder and continue to Atomic Attributes

# Atomic Attributes: Select basis set

Select the default def-SV(P) basis set

Workflow: Geometry → **Atomic Attributes** → Molecular Attributes → Method → Start Job → Results

Charge: Use from input

Basis Sets

Basis Functions 34

Basis Set for all Atoms: def-SV(P)

Basis for elements:

- C: def-SV(P)
- O: def-SV(P)
- H: def-SV(P)

Basis for individual Atoms

Num...	Eleme...	Basis set	ECP	Mass	Nuclear char...	Basis funcio...
1	O	def-SV(P)		15.9994	8	15
2	C	def-SV(P)		12.0110	6	15
3	H	def-SV(P)		1.0079	1	2
4	H	def-SV(P)		1.0079	1	2

<< Previous

Continue >>

Continue to Molecular Attributes

# Molecular Attributes: Generate initial guess MOs

Generate initial MOs by doing an extended Hückel calculation

The screenshot shows the TmoleX 4.1 (client) - qc\_int interface. The main window displays a workflow diagram with steps: Geometry, Atomic Attributes, Molecular Attributes (highlighted in red), Method, Start Job, and Results. Below the diagram, the 'Molecular Orbitals' section is active, showing a table with columns: No, Spin, Sym., Energy(Ha...), Energy[eV], and HOMO/LU... The 'Generate MOs' button is highlighted in red. A dialog box titled 'Perform an extended Hückel calculation' is overlaid on the interface, displaying the following information:

**Perform an extended Hückel calculation**

Symmetry: C1  
Charge: 0.0  
Unpaired electrons: 0.0

FHT AOs

C:	3P(DZ)
O:	3P(DZ)
H:	2S(DZ)

OK Cancel

Continue to Method

# Method: Define your method

Select the default method (ri-dft BP86/m3)

The screenshot shows the TmoleX 4.1 (client) - qc\_int interface. The workflow is displayed at the top, with the 'Method' step highlighted in yellow. Below the workflow, the 'Level of Theory' section is active, showing 'DFT' selected. The 'DFT settings' section shows 'Functional' set to 'BP86' and 'Gridsize' set to 'm3'. The 'COSMO' section has 'Activate' unchecked. The 'Two component treatment' section has 'Activate', 'Kramers', and 'complex DIIS' all unchecked. The 'Auxiliary basis sets for RI-J' table is visible on the right.

Element	Basis set	Auxiliary basis set
C	def-SV(P)	def-SV(P)
O	def-SV(P)	def-SV(P)
H	def-SV(P)	def-SV(P)

Continue to Start Job

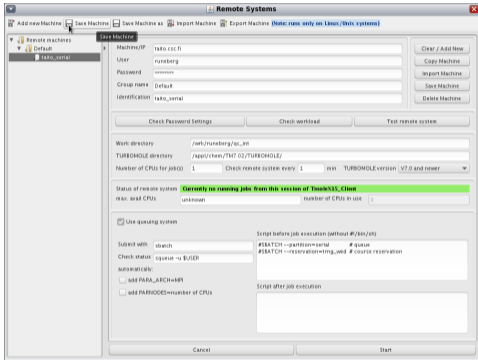
# Start Job: Define your job type

We want to do a geometry optimization of the ground state

The screenshot shows the TmoleX 4.1 (client) - qc\_int interface. The main window displays a workflow from Geometry to Start Job. The 'Start Calculation' dialog is open, showing the 'Job type' section with 'Geometry Optimization' selected, and 'Ground state' chosen. The 'Method' section is configured with Level: DFT, Functional: b-p, Basis set: def-SVP, and Symmetry: C1. The 'Options' section shows convergence criteria: Energy  $10^{-11}$  Hartree, Gradient norm 3  $|dE/dxyz| = 10^{-11}$  Hartree/Bohr, and Max. no. of cycles 50. The 'Use resources' section shows Memory used for 1 MB, Disk 1 MB for HF, and No. of CPUs 1. The 'Save and Run' section has buttons for 'Run (local)', 'Save', and 'Run (network)'. The 'Run (network)' button is highlighted.

Continue to Run(network)

# Run(network): Setup remote job



Save Settings and Start

Machine/IP: taito.csc.fi

User: trngXX

Work directory: /wrk/trngXX/qc\_int

TURBOMOLE directory: /appl/chem/TM7.1/TURBOMOLE

Submit with: sbatch

Check status: squeue -u \$USER

Script before job execution:

```
#SBATCH --partition=serial
```

```
#SBATCH --reservation=trng_wed
```

# Run(network): Job starts

The screenshot displays the TmoleX 4.1 (client) - qc\_int interface. The top status bar shows 'Jobs running: local: 0/4, remote: 1' and 'Memory used for TmoleX: 49.0/64.9 MB'. The main workflow area includes steps: Geometry, Atomic Attributes, Molecular Attributes, Method, and Start Job. Below this is a 'Jobs' table with one entry:

ID	Name	Type	Start	Stop	Machine
1	job_GEO_1	GEO,DFT/RII,B-P,charge 0,C1,def-SVC...	Mar 2, 2016 9:0...	Running	taito.csc.fi

At the bottom right, there is a plot titled 'Energy vs. Geometry cycle' with a y-axis from 0.00 to 1.00 and an x-axis from 0.0 to 1.0. The plot area is currently empty.

# Results:

The geometry optimization needed 5 cycles to reach the stationary point on the energy surface

The screenshot displays the TmoleX 4.1 (client) - qc\_int interface. The main window shows the job results for a Geometry Optimization. The status is 'Converged' and the HOMO-LUMO gap is 3.728 eV. The convergence criteria are shown as follows:

**Geometry Convergence Criteria**

\$convinfo  
energy change : actual value = -0.4453E-06 threshold = 0.1000E-05  
geom. gradient : actual value = 0.2801E-04 threshold = 0.1000E-02

**Energy**

total energy = -114.41873721126  
-----  
kinetic energy = 113.44915075231  
potential energy = -227.86788796357

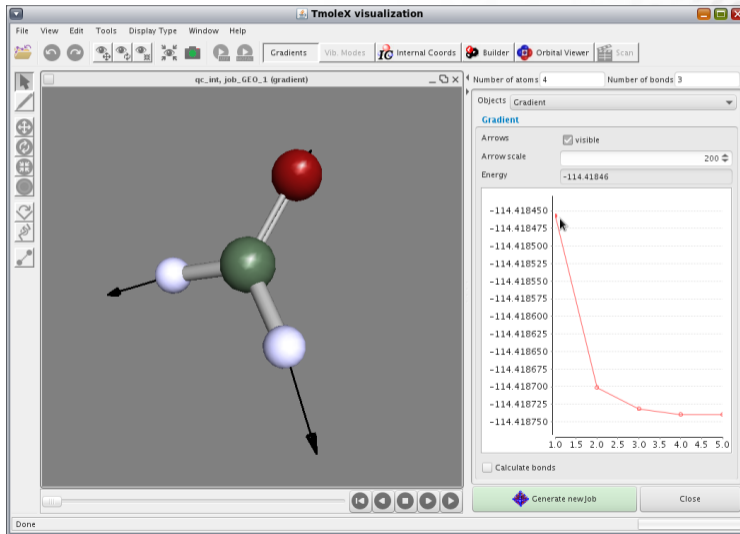
**Gradients**

cycle	SCF energy	dE/dxyz
1	-114.4184569894	0.016886
2	-114.4187043913	0.006723
3	-114.4187321508	0.002025
4	-114.4187367567	0.000444
5	-114.4187372020	0.000052

The interface also shows a workflow diagram at the top with steps: Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. The 'Job Results' section is currently selected, showing the convergence status and energy values. The 'Open views' section on the right includes options for Orbital/Density Plot, Gradients, Vibrations, Thermochemical Properties, Population Properties, NMR Shieldings, and View.cosmo File. The 'Open Files' section includes Output, Energy, Moments, UV/Vis Spectrum, CD Spectrum, Raman Spectrum, and IR Spectrum.

# Results: Gradients

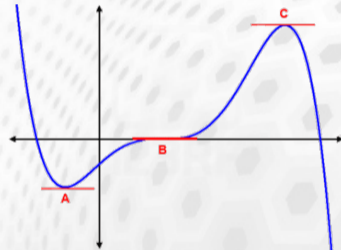
The length of the arrows show how steep the energy surface is in that direction



# Results: Gradients

At the end of the geometry optimization we have reached a stationary point (gradient smaller than a given threshold) that could correspond to:

- ▶ a minimum **A**
- ▶ an inflection point **B**
- ▶ a maximum **C**



The nature of the stationary point can be deduced from the curvature (Hessian). A positive curvature corresponds to a minimum, a negative to a maximum.

# Vibrational spectrum

In order to verify that the stationary point is a true minimum (positive curvature in all directions = positive frequencies) do a frequency calc (Reuse data by just hitting "Start new job by using current data as input" )

The screenshot shows the TmoleX 4.1 (client) - qc\_int interface. The main window displays the job results for a frequency calculation. The job name is 'job\_CEO\_1'. The results are as follows:

```
Job Results
-----
rho
y change : actual value = -0.4453E-06 threshold = 0.1000E-05
i gradient : actual value = 0.2801E-04 threshold = 0.1000E-02

gy
energy = -114.41873721126
-----
c energy = 113.44915075231
tial energy = -227.86788796357

ients
s = 1 SCF energy = -114.4184569894 |dE/dxyz| = 0.016886
s = 2 SCF energy = -114.4187043913 |dE/dxyz| = 0.006723
s = 3 SCF energy = -114.4187321508 |dE/dxyz| = 0.002025
s = 4 SCF energy = -114.4187367567 |dE/dxyz| = 0.000444
s = 5 SCF energy = -114.4187372020 |dE/dxyz| = 0.000052
```

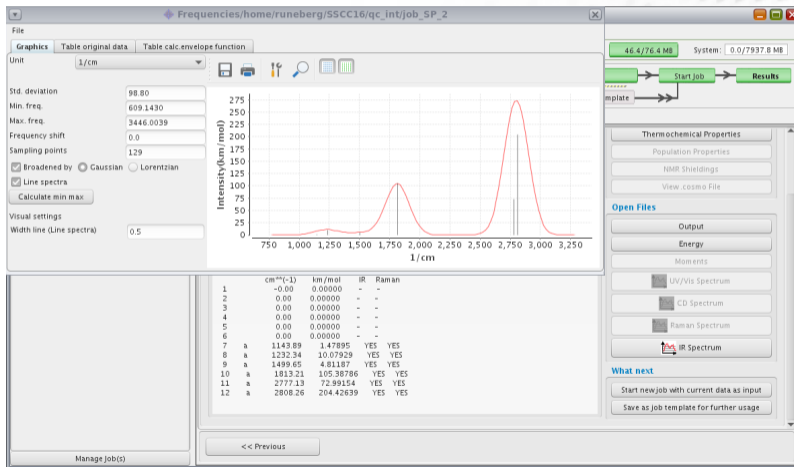
The interface also shows a 'What next' section with two buttons: 'Start new job with current data as input' and 'Save as job template for further usage'. The 'Start new job with current data as input' button is highlighted with a mouse cursor.

# Vibrational spectrum

The screenshot shows the TmolX 4.1 (client) - qc\_int interface. The top menu bar includes File, Edit, Templates, Results, Extras, Tools, and Help. The status bar shows 'Jobs running local: 0/4 remote: 0' and 'Memory used for TmolX: 58.8/78.7 MB System: 0.0/75'. The main workflow consists of Geometry, Atomic Attributes, Molecular Attributes, Method, Start Job, and Results. A 'Start Calculation' dialog is open, showing the 'Job type' section with 'Spectra & Excited States' selected. A dropdown menu is open under 'Spectra & Excited States', listing options: 'IR & vibrational frequencies' (selected), 'UV/Vis and CD(vertical excitations)', 'NMR shieldings', 'Raman & vibrational frequencies', 'Optical rotations / dynamic polarizability', and 'Static polarizability'. The 'Method' section shows 'Level: DFT' and 'Functional: b-p'. The 'Options' section shows 'Convergence criteria' with 'Energy' set to  $6 \times 10^{-11}$  Hartree, 'Gradient norm' set to  $3 |dE/dxyz| = 10^{-11}$  Hartree/Bohr, and 'Max. no. of cycles' set to 50. The 'USE resources' section shows 'Memory used for' set to 1 MB, 'Disk' set to 1 MB for HF, and 'No. of CPUs' set to 1. The 'Save and Run' section has buttons for 'Run (local)', 'Save', and 'Run (network)'. The 'Manage Job(s)' button is at the bottom left.

# Results: Frequency calculation

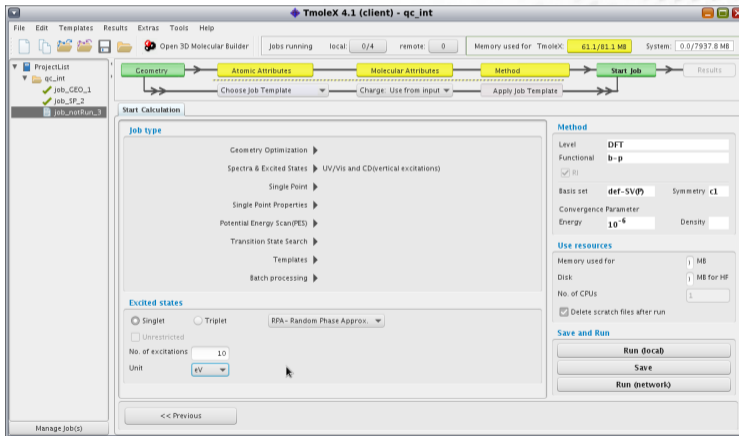
All calculated frequencies are positive indicating that the structure corresponds to a true minimum.



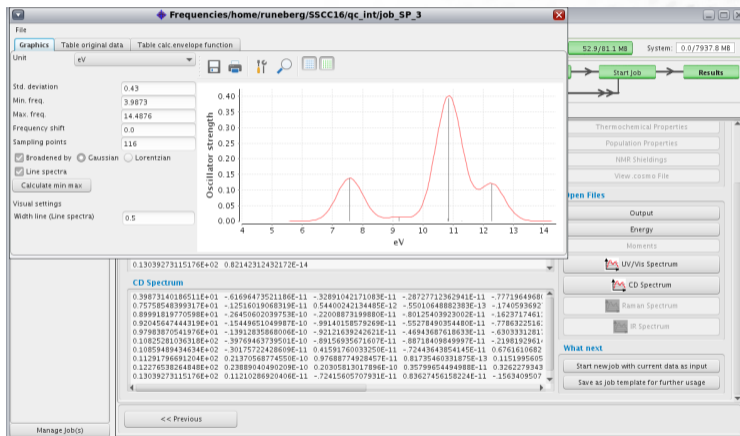
# Task 2: Vertical absorption spectrum of the ground state

"Start Job" -> "Spectra & Excited states"

Do for singlet states and 10 excitations



# Spectra & Excited states



## Task 3: Identify and characterize the first excited state

Check output for the lowest excitation  $E^{\text{abs}}$  and the type of excitation this corresponds to

```
TextViewer - escf.out
File Edit

1 singlet a excitation

Total energy:                0.1465310340469408
Excitation energy:           0.1465310340469408
Excitation energy / eV:      3.987314018651063
Excitation energy / nm:      310.9467762672303
Excitation energy / cm^-1:   32159.84458354145

Oscillator strength:
  velocity representation:    0.5215757899036950E-15
  length representation:      0.2185914223305519E-15
  mixed representation:       0.3376566191450008E-15

Rotatory strength:
  velocity representation:    0.5802037506757178E-17
  velocity rep. / 10^(-40)erg*cm^3: 0.3748395679062240E-12
  length representation:      -0.9549825686869016E-16
  length rep. / 10^(-40)erg*cm^3: -0.6169647352118631E-11

Dominant contributions:
  occ. orbital energy / eV    virt. orbital energy / eV    |coeff.|^2*100
  8 a      -6.11              9 a      -2.38              100.0

Change of electron number:
```

# Spectra & Excited states

**Choose Molecular Orbital(s)**

Sel.	No.	Spin	Sym.	Energy[Hartree]	Deg.	Occ.	HOMO/LUMO	quick	high...
<input type="checkbox"/>	12	ab	12a	0.1705	1	0	LUMO + 3		
<input type="checkbox"/>	11	ab	11a	0.1121	1	0	LUMO + 2		
<input type="checkbox"/>	10	ab	10a	0.0463	1	0	LUMO + 1		
<input checked="" type="checkbox"/>	9	ab	9a	-0.0875	1	0	LUMO		
<input checked="" type="checkbox"/>	8	ab	8a	-0.2245	1	2	HOMO		
<input type="checkbox"/>	7	ab	7a	-0.3665	1	2	HOMO - 1		
<input type="checkbox"/>	6	ab	6a	-0.3957	1	2	HOMO - 2		
<input type="checkbox"/>	5	ab	5a	-0.4395	1	2	HOMO - 3		
<input type="checkbox"/>	4	ab	4a	-0.5652	1	2	HOMO - 4		

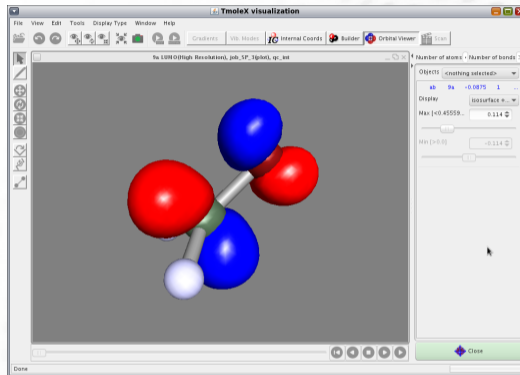
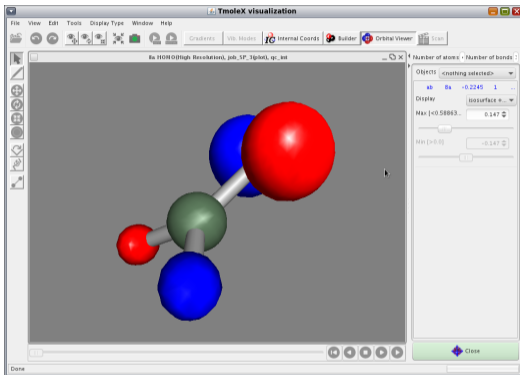
**Choose Density and Electrostatic Properties**

Sel.	Plot-propertyname	Plot-filename	quick	high-res
<input type="checkbox"/>	Electrostatic potential	tp		
<input type="checkbox"/>	Electric field	tf		
<input type="checkbox"/>	Gradient of electric field	tg		
<input type="checkbox"/>	Electrostatic potential color-coded on den...	tp_td		

View all in one           

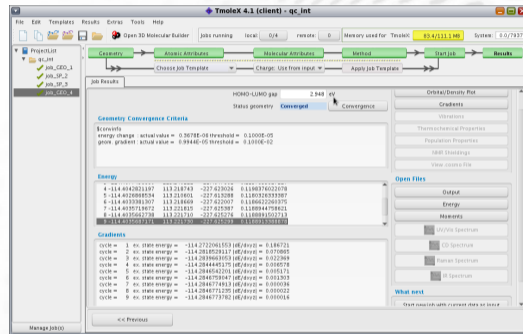
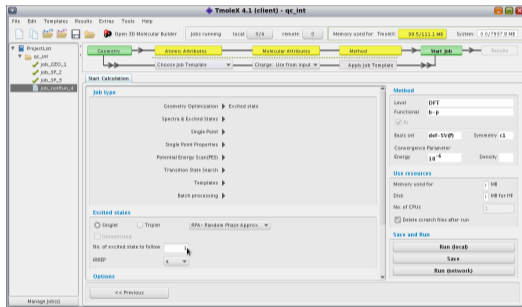
Select the relevant "8a" and "9a" orbitals

# Relevant orbitals



The "8a" HOMO orbital corresponds to a non-bonding ( $n$ ) electron pair on oxygen. The "9a" LUMO orbital corresponds to an antibonding ( $\pi^*$ ) orbital between oxygen and carbon. The lowest vertical excited state is the  $n \rightarrow \pi^*$  we are interested in.

# Task 4: Optimize the excited state structure



The geometry optimization converged to a stationary point but is it a true minimum?

# NumForce

TmoleX is not capable of doing NumForce calc's. Hence we need to copy yhe optimized structure to taito-shell and do the Numforce from command line.

```
runeberg@vihertikka:~/SSCC16/qc_int
[runeberg@vihertikka qc_int]$ scp -r job_GEO_4/ taito-shell.csc.fi:/wrk/runeberg/
kill-job                100% 1020    1.0KB/s  00:00
start-job.out          100%  28     0.0KB/s  00:00
Job_Ended              100%  0       0.0KB/s  00:00
GEO_OPT_CONVERGED     100% 1171    1.1KB/s  00:00
message.output         100%  0       0.0KB/s  00:00
slurm-8607810.out      100%  406    0.4KB/s  00:00
job.start              100%  772    0.8KB/s  00:00
auxbasis               100% 1784    1.7KB/s  00:00
start-job              100%  870    0.9KB/s  00:00
coord                  100% 1419    1.4KB/s  00:00
job.last               100%  57KB   56.6KB/s 00:00
energy                 100%  758    0.7KB/s  00:00
mos                    100% 23KB    23.1KB/s 00:00
gradient               100% 5764    5.6KB/s  00:00
converged              100%  321    0.3KB/s  00:00
basis                  100% 1067    1.0KB/s  00:00
control                100% 2027    2.0KB/s  00:00
[runeberg@vihertikka qc_int]$ ssh taito-shell.csc.fi -l runeberg
```

```
runeberg@c308:/wrk/runeberg/job_GEO_4
To see which node(s) your jobs in Taito-Shell are running on, run:
  squeue -M shell -l -u $USER

-- Software --
Available modules can be listed with command: module avail | module spider
-- News --

2015-05-25: Changed default slurm instance to Taito's. For example
  srun now submits jobs to Taito's partitions, like parallel
  instead of the oversubscribed.

[runeberg@c308 ~]$ cd /wrk/runeberg/job_GEO_4/
[runeberg@c308 job_GEO_4]$ ls
auxbasis  coord      Job_Ended  message.output  slurm-8607810.out
basis     energy     job.last   mos              start-job
control   GEO_OPT_CONVERGED  job.start  numforce         start-job.out
converged gradient    kill-job   slurm-8561347.out
[runeberg@c308 job_GEO_4]$ module load turbomole
Turbomole version 7.02 environment loaded
Get an example job script with the command:
wget http://extras.csc.fi/chem/progs/turbomole/job-tm702-taito.job
[runeberg@c308 job_GEO_4]$ cpc numforce
```

Copy directory: `scp -r job_GEO_4 taito-shell:/wrk/<username>`

Login: `ssh -X taito-shell -l <username>`

Go to directory: `cd /wrk/<username>/job_GEO_4`

# NumForce

```
runeberg@c308:wrk/runeberg/job_GEO_4
2015-05-25: Changed default slurm instance to Taito's. For example
srun now submits jobs to Taito's partitions, like parallel
instead of the oversubscribed.

[runeberg@c308 ~]$ cd /wrk/runeberg/job_GEO_4/
[runeberg@c308 job_GEO_4]$ module load turbomole
Turbomole version 7.02 environment loaded
Get an example job script with the command:
wget http://extras.csc.fi/chem/progs/turbomole/job-tm702-taito.job
[runeberg@c308 job_GEO_4]$ cpc numforce
File control is copied to numforce
File coord is copied to numforce
File job_notRun_1.cosmo does not exist
File basis is copied to numforce
File forceapprox does not exist
File auxbasis is copied to numforce
File gradient is copied to numforce
File coord is copied to numforce
File mos is copied to numforce
File energy is copied to numforce
File optinfo does not exist
File hessapprox does not exist
[runeberg@c308 job_GEO_4]$
```

```
runeberg@c308:wrk/runeberg/job_GEO_4/numforce
srun now submits jobs to Taito's partitions, like parallel
instead of the oversubscribed.

[runeberg@c308 ~]$ cd /wrk/runeberg/job_GEO_4/
[runeberg@c308 job_GEO_4]$ module load turbomole
Turbomole version 7.02 environment loaded
Get an example job script with the command:
wget http://extras.csc.fi/chem/progs/turbomole/job-tm702-taito.job
[runeberg@c308 job_GEO_4]$ cpc numforce
File control is copied to numforce
File coord is copied to numforce
File job_notRun_1.cosmo does not exist
File basis is copied to numforce
File forceapprox does not exist
File auxbasis is copied to numforce
File gradient is copied to numforce
File coord is copied to numforce
File mos is copied to numforce
File energy is copied to numforce
File optinfo does not exist
File hessapprox does not exist
[runeberg@c308 job_GEO_4]$ cd numforce/
[runeberg@c308 numforce]$ NumForce -ri -ex 1 &> NumForce.out&
```

Windows users should issue the command: `dos2unix *`

Load turbomole environment: `module load turbomole`

Copy inputs to a new directory: `cpc numforce`

Go to new directory: `cd numforce`

Start NumForce: `NumForce -ri -ex 1 &> NumForce.out&`

Check results: `cat vibspectrum`

# NumForce

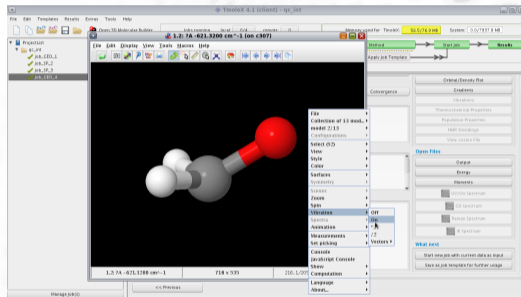
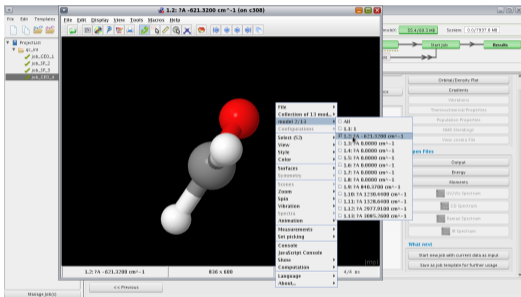
Since there is one imaginary frequency (negative force constant) the stationary structure is not a minimum but a saddle point. Use Jmol to analyze what kind of motion the imaginary frequency corresponds to.

```
runeberg@c308:/wrk/runeberg/job_GEO_4/numforce
RAMAN      -      YES      YES      YES      YES      YES
#####
#          END OF NumForce          #
#####
date: Wed Mar 2 22:17:29 EET 2016
[runeberg@c308 numforce]$ cat vibspectrum
$ vibrational spectrum
# mode      symmetry      wave number      IR intensity      selection rules
#          cm**(-1)      km/mol           IR      RAMAN
1          a          -621.32          0.00000          YES      YES
2          -          -0.00           0.00000          -        -
3          0          0.00            0.00000          -        -
4          0          0.00            0.00000          -        -
5          0          0.00            0.00000          -        -
6          0          0.00            0.00000          -        -
7          0          0.00            0.00000          -        -
8          a          840.37          4.28662          YES      YES
9          a          1230.44         32.87044         YES      YES
10         a          1328.64         0.11242          YES      YES
11         a          2977.91         13.33541         YES      YES
12         a          3085.26         7.52101          YES      YES
$end
[runeberg@c308 numforce]$
```

```
runeberg@c308:/wrk/runeberg/job_GEO_4/numforce
#####
#          END OF NumForce          #
#####
date: Wed Mar 2 22:17:29 EET 2016
[runeberg@c308 numforce]$ cat vibspectrum
$ vibrational spectrum
# mode      symmetry      wave number      IR intensity      selection rules
#          cm**(-1)      km/mol           IR      RAMAN
1          a          -621.32          0.00000          YES      YES
2          -          -0.00           0.00000          -        -
3          0          0.00            0.00000          -        -
4          0          0.00            0.00000          -        -
5          0          0.00            0.00000          -        -
6          0          0.00            0.00000          -        -
7          0          0.00            0.00000          -        -
8          a          840.37          4.28662          YES      YES
9          a          1230.44         32.87044         YES      YES
10         a          1328.64         0.11242          YES      YES
11         a          2977.91         13.33541         YES      YES
12         a          3085.26         7.52101          YES      YES
$end
[runeberg@c308 numforce]$ aoforce2g98 numforce/aoforce.out > g98.out
[runeberg@c308 numforce]$ module load jmol
Jmol version 14.2 is now in use
[runeberg@c308 numforce]$ jmol g98.out
```

Convert from aoforce to g98 : `aoforce2g98 numforce/aoforce.out > g98.out`  
load the Jmol environment: `module load jmol`

Launch Jmol using the data in g98.out: `jmol g98.out`

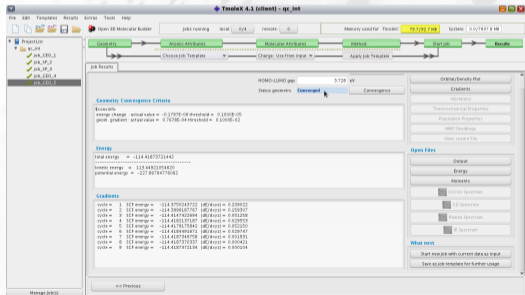
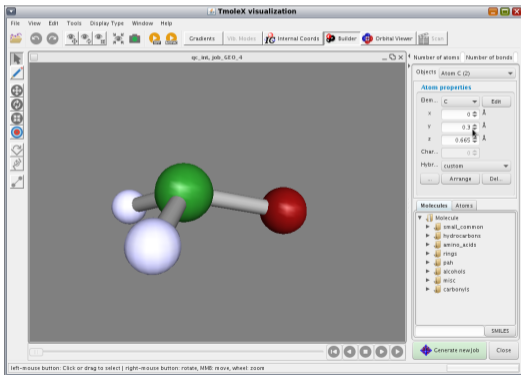


Select the imaginary frequency: `model 1/13`

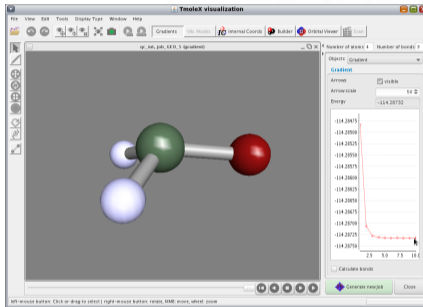
Activate animation: `Vibration: On`

# Excited state optimization, new try

Since the mode corresponds to an umbrella motion where the planar structure is balancing on the ridge of folding the umbrella either left or right) we want to distort the new starting structure in that direction. Open the 3D Builder, select the carbon atom and distort it in the y-direction. Then redo the optimization.



From the "Gradients" menu confirm that this is a new stationary point corresponding to a pyramidal structure



Copy the new optimized structure to taito-shell and redo the Numforce.

Copy directory: `scp -r job_GEO_5 taito-shell:/wrk/<username>`

Login: `ssh -X taito-shell -l <username>`

Go to directory: `cd /wrk/<username>/job_GEO_5`

# NumForce

```
runeberg@c307:wrk/runeberg/job_GEO_5/numforce
[runeberg@c307 runeberg]$ cd job_GEO_5/
[runeberg@c307 job_GEO_5]$ module load turbomole
Turbomole version 7.02 environment loaded
Get an example job script with the command:
wget http://extras.csc.fi/chem/progs/turbomole/job-tm702-taito.job
[runeberg@c307 job_GEO_5]$ cpc numforce
File control is copied to numforce
File coord is copied to numforce
File job_notRun_1.cosmo does not exist
File basis is copied to numforce
File forceapprox does not exist
File auxbasis is copied to numforce
File gradient is copied to numforce
File coord is copied to numforce
File mos is copied to numforce
File energy is copied to numforce
File optinfo does not exist
File hessapprox does not exist
[runeberg@c307 job_GEO_5]$ cd numforce/
[runeberg@c307 numforce]$ NumForce -ri -ex 1 &> Numforce.out
```

```
runeberg@c307:wrk/runeberg/job_GEO_5/numforce
File optinfo does not exist
File hessapprox does not exist
[runeberg@c307 job_GEO_5]$ cd numforce/
[runeberg@c307 numforce]$ NumForce -ri -ex 1 &> Numforce.out&
[1] 19592
[runeberg@c307 numforce]$ cat vibspectrum
$ vibrational spectrum
# mode symmetry wave number IR intensity selection rules
# cm**(-1) km/mol IR RAMAN
1 -0.00 0.00000 - -
2 -0.00 0.00000 - -
3 -0.00 0.00000 - -
4 0.00 0.00000 - -
5 0.00 0.00000 - -
6 0.00 0.00000 - -
7 a 732.06 53.90179 YES YES
8 a 875.25 5.22147 YES YES
9 a 1229.08 36.02499 YES YES
10 a 1335.56 2.07743 YES YES
11 a 2868.53 2.46759 YES YES
12 a 2952.71 0.18470 YES YES
Send
[1]+ Done NumForce -ri -ex 1 &>Numforce.out
[runeberg@c307 numforce]$
```

Load turbomole environment: `module load turbomole`

Copy inputs to a new directory: `cpc numforce`

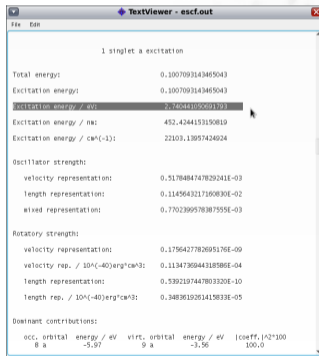
Go to new directory: `cd numforce`

Start NumForce: `NumForce -ri -ex 1 &> NumForce.out&`

Check results: `cat vibspectrum`

## Task 5: Calculate the emission spectrum of the first excited state

The optimized excited state geometry corresponds to a true minimum. At that geometry, redo the excitation spectrum "Start Job" -> "Spectra & Excited states"  
Do it for singlet states and 10 excitations



```
1 singlet a excitation

Total energy:          0.1007093143465043
Excitation energy:     0.1007093143465043
Excitation energy / eV: 2.740441050691793
Excitation energy / na: 452.4244153150819
Excitation energy / cm^(-1): 22103.13957424924

Oscillator strength:
  velocity representation: 0.5178484747829241E-03
  length representation:   0.1145643217100830E-02
  mixed representation:    0.7702399578387555E-03

Rotatory strength:
  velocity representation: 0.1756427782695176E-09
  velocity rep. / 10^(-40)erg^3cm^3: 0.1134736944318586E-04
  length representation:   0.5392197447803320E-10
  length rep. / 10^(-40)erg^3cm^3: 0.3483619261415833E-05

Dominant contributions:
  occ. orbital energy / eV  virt. orbital energy / eV  |coeff.|^2*100
  8 a      -5.97          9 a      -3.56          100.0
```

# Results

- ▶ Tabulate all relevant data such as  $R^{GS}$ ,  $R^{ES}$ ,  $E^{GS}$ ,  $E^{ES}$ , as well as  $E^{abso}$ ,  $E^{fluo}$ ,  $E^{adia}$  and  $E^{adia}_{ZPVE}$
- ▶ Compare your results with experimental data found in the literature
- ▶ Compare your results with computational results obtained at more sophisticated levels of theories
- ▶ If you have time, apply the efficient ricc2 implementation in Turbomole on the system
- ▶ If you have time, extend the study to include solvent effects (COSMO)

# Possible issues?

- ▶ Is the basis set sufficient?
- ▶ What is the ultimate choice of functional?
- ▶ For this particular physical problem is tddft the method of choice?
- ▶ How does the environment interact?
- ▶ Should we be more careful when treating dispersion (intra, inter)?
- ▶ Relativity?
- ▶ Temperature and dynamics?