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APPENDIX 2

Density Functional Theory Calculation of Vibrational Frequencies with Gaussian[©] 98W¹

(Courtesy of Dr. Mircea Gheorghiu. Used with permission.)

This appendix describes the use of Gaussian 98W software for calculating vibrational frequencies for the isotopomers of acetylene. We will use Gaussian 98 to perform Density Functional Theory (DFT) calculations that solve the full molecular Hamiltonian for acetylene and from the computed potential energy surface derive the normal mode vibrational frequencies. These will be compared with your experimental values.

1. Building C₂H₂

The Gaussian 98W DFT calculation requires an initial structure that is contained in Cartesian coordinates in an input file. The structure can be built interactively with the GaussView, which saves the input file.

To start GaussView:

Click on **Shortcut to gview**. In GaussView, there are three windows design to assist you in building the geometry for the input file: (i) **GaussView 2.1**, (ii) **Builder** and (iii) **View1** (see Fig.1).

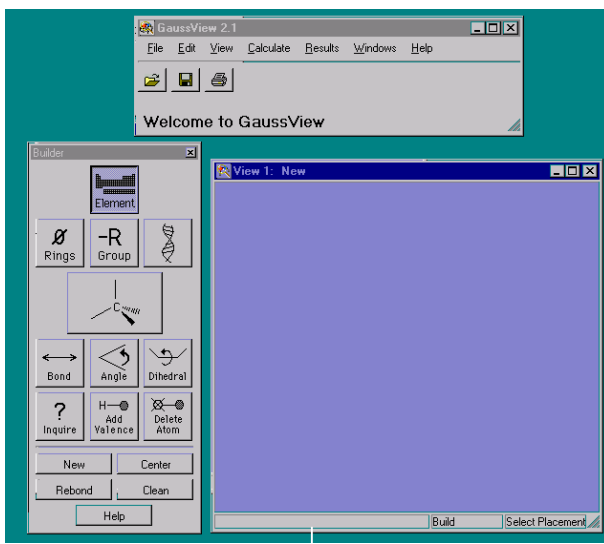


Figure 1 – Initial Windows in GaussView

Screenshot images courtesy of Gaussian, Inc. Used with permission.

¹ **Gaussian[©] 98W**, Version 5.4, is a computational package of *Gaussian Inc.*, 18401 Carnegie Office Park., Bldg. 6, Pittsburg, PA 15106.

Click on the **-R Group** button from the **Builder** window and the larger fragment button directly beneath it. The **Select -R Group Fragment** window will appear. Choose the **CH≡C-** group; the same **CH≡C-** group will appear in the fragment button under the **-R Group** button. The **Group Fragment** window closes automatically.

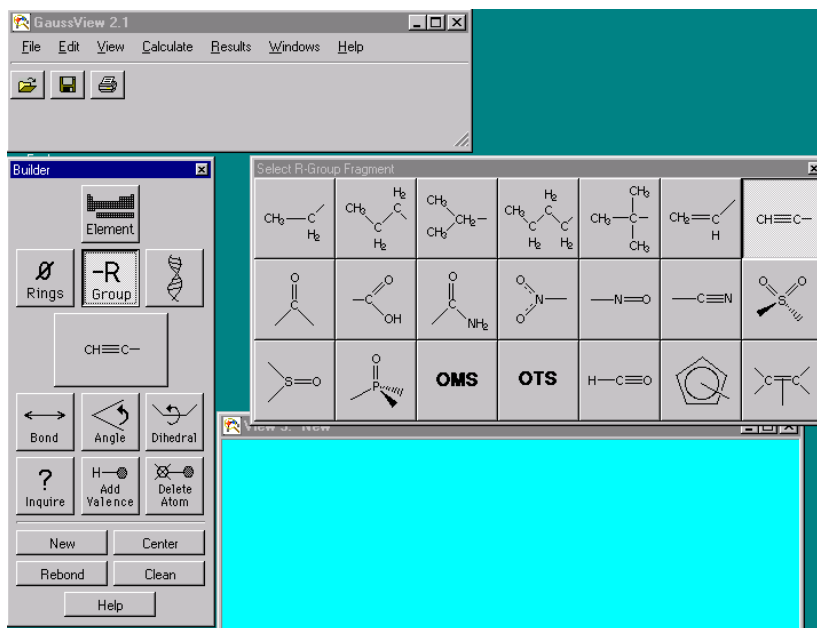


Figure 2. Group Fragment Windows in GaussView

To build the acetylene structure, now click anywhere in the **View** window. The ball-and-stick structure for acetylene is displayed. Press the **Center** button if it is necessary.

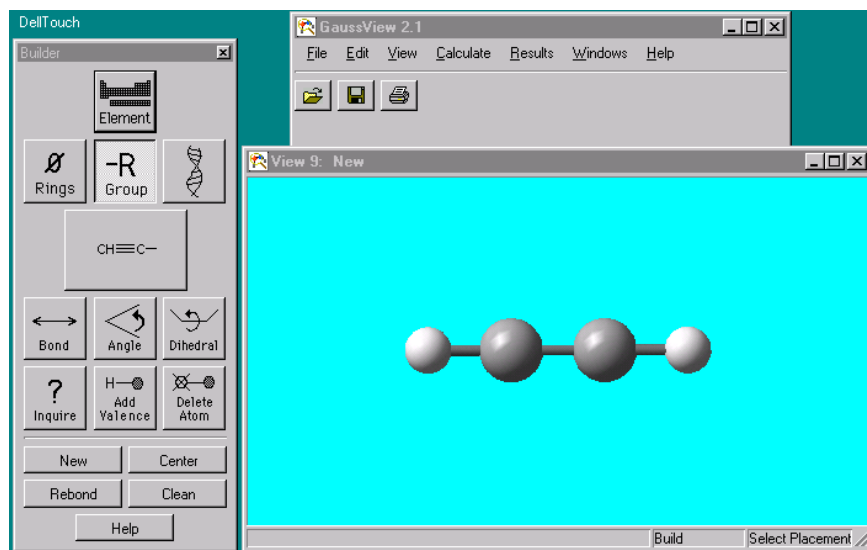


Figure 3 – Acetylene Structure

Screenshot images courtesy of Gaussian, Inc. Used with permission.

2. Calculation Setup

Now you have created the starting structure, and you need to setup calculation parameters and define the level of theory used.

Click on **Calculate** and then **Gaussian** (in the **GaussView 2.1** window) to bring up the **Gaussian Calculation Setup** window. In the **Title** window, type a title of your choice to identify the calculation. Set the **Charge** to **0** and the **Spin** to **singlet**. In the **Job Type** window choose the type of calculation as **Opt+Freq**. This will perform a geometry optimization followed by a vibrational frequency calculation. Also, make sure that **No Raman Intensities** is selected to speed up the calculation. In the **Method** window choose the following to define the level of theory: **Ground state**, **B3LYP**, **Restricted**, Basis set: **6-311G**. In the **Solvation** window, choose **none**. In the **General Options** window, be sure that **all of the boxes are unchecked!**

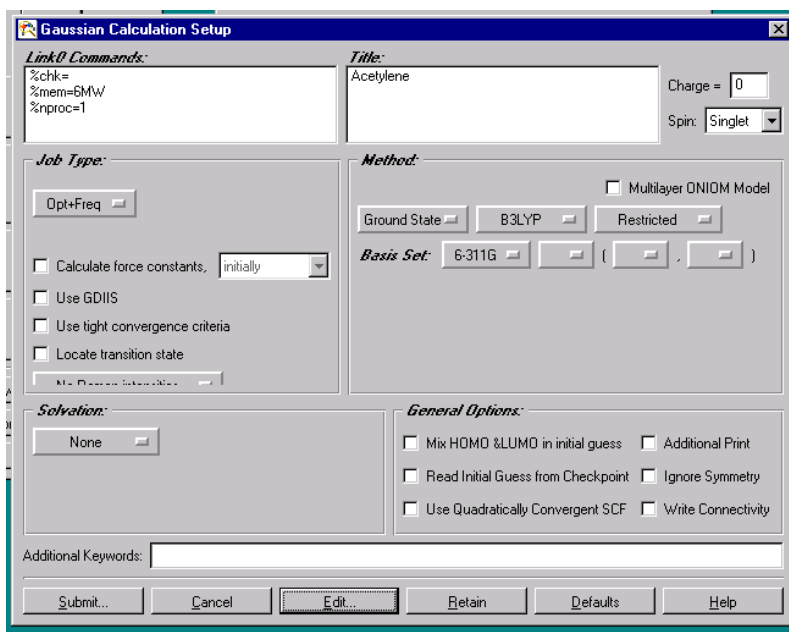


Figure 4 – Calculation Setup Window

3. Editing the Input File

The built molecular structure and the options in the setup window are used to generate a setup file that contains the parameters for the calculation. You can now edit this input file to setup an interactive calculation of all three isotopomers.

To edit the input file, click on the **Edit..** button and follow the instructions for first saving the input file. The input file will then appear in a **Notepad** window. The first lines in the input file beginning with **%** define calculation variables. The line beginning with **#**

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is the routing section that defines the calculation to be performed through a series of keywords.

```
%mem=6MW
%nproc=1
%chk=C2H2_C2HD_C2D2_B.chk
# opt freq=noraman rb3lyp/6-311g

Acetylene

0 1
C      0      1.158407      -0.386660      -1.433525
C      0      1.158407      -0.386660      21
H      0      X1      -0.386660      22
H      0      X2      Y1      23

21      -0.238525
22      -2.494525
23      0.822475
X1      1.158407
X2      1.158407
Y1      -0.386660
```

Figure 5 – The input file for the C₂H₂ molecule.

Keywords:

- **#** (pound sign) initiates the route section of a Gaussian 98W job. A blank line must terminate the route section. **#T** is for a terse output file, which limits the output to essential information and results. You should set this option by typing a “T” after the pound sign.
- **opt**: geometry optimization is performed. The geometry will be adjusted until a stationary point is found on the potential surface. The default algorithm is Berny algorithm using redundant internal coordinates.²
- **freq=noraman** skips the extra steps (therefore, saving computation time) required to compute the Raman intensities during analytic frequency calculations.
- **b3lyp**: the Becke³ three parameter functional combined with the local and non-local terms provided by Lee, Yang, and Parr⁴.
- **6-311G** is a split-valence basis set. The inner-shell basis functions are written in terms of six Gaussians. Each valence-shell basis function is split in three parts, written in terms of three, one and one Gaussians.

Screenshot images courtesy of Gaussian, Inc. Used with permission.

² Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comp. Chem.* **1996**, *17*, 49.

³ Becke, A. D. *J. Chem. Phys.*, **1996**, *104*, 1040.

⁴ Lee, C.; Yang, W.; Parr, R. G., *Physical Revue B* **1988**, *37*, 785.

The DFT calculations for the three isotopomers (C_2H_2 , C_2HD and C_2D_2) can be submitted from a single input file, by editing it for a multi-step job. Edit the input file as illustrated below:

```

X1          1.158407
X2          1.158407
Y1         -0.386660

--Link1--
%chk=C2H2_C2HD_C2D2_B.chk
#T opt freq=noraman rb3lyp/6-311g Geom=Check Guess=Read freq=ReadIsotopes

Mono-deuterated acetylene

0 1

300.0  1.0
12
12
2
1

--Link1--
%chk=C2H2_C2HD_C2D2_B.chk
%NoSave
#T opt freq=noraman rb3lyp/6-311g Geom=Check Guess=Read freq=ReadIsotopes

Bis_deuterated acetylene

0 1

300.0  1.0
12
12
2
2

```

Figure 6 – Editing Input File for Multiple Calculations

The first three lines in Fig. 6 (X1, X2, Y1) are the last three lines from the original input file in Fig. 5. Afterward the file is edited to add the following lines:

- The input of job #1 is separated from the input file of job #2 by a separate line **--link1--** which is preceded by a blank line. Job #3 is similarly separated from job #2.
- The second line is the **%chk** command which specifies the checkpoint file. In Gaussian this is a scratch file that is normally deleted automatically after the job is finished, so you can use the same file name for all three jobs. Type (or copy) this line with the checkpoint file name exactly as at the top of your first calculation.
- Now enter the routing section. In addition to the parameters in job #1, add some additional keywords. First, we tell the second calculation to retrieve the already optimized geometry from the previous check point file with **Geom=Check**. The **Guess** keyword controls the initial guess for the wavefunction (SCF initial guess); for **Guess=Read**, it is read from the checkpoint file. **Freq** is the keyword for to calculate the force constants and the resulting vibrational frequencies. Vibrational frequencies are computed only at the stationary point. The **ReadIsotopes** option is used to specify the

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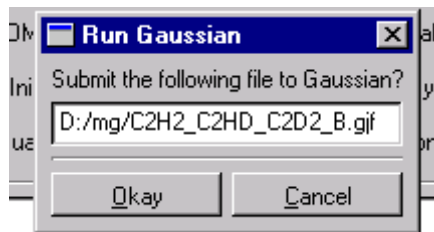
temperature, pressure and isotopes for thermochemical analysis. (The parameters for the ReadIsotopes option are listed later in the file (following the “0” and “1” which define the charge and spin). In Fig. 6, for the second job, we have to enter a temperature of 300 °K, pressure of 1 atm, and the isotope mass for carbons, $m_C=12$, for deuterium, $m_D=2$, and hydrogen $m_H=1$. The masses are entered in the same order as the atoms in the original job of the input file. In the third job (bis-deuterated acetylene) the second hydrogen has been changed into deuterium, $m_D=2$.)

- A blank line follows each route line.
- Next is the **Title** line, which we use to identify the job. After another blank line, we enter the **charge** of zero and the **multiplicity** of 1. After another blank line, the **ReadIsotopes** information is typed.

The information entered for job#2 can be copied to the end of the file and edited to set the parameters for job#3, the bis-deuterated acetylene. Be sure to change the title line and the isotopes. Additionally, after the **%chk=...** line, add a separate line with the **%NoSave** keyword. The **%NoSave** command deletes the checkpoint file after the completion of job #3. Be sure to terminate the final job with two blank lines.

4. Running the Calculation and Reading the Output File

You have now created the input file that will run all three isotopomers of acetylene. Save the input file to the **D:/GaussView/5.33** directory, with the same name as the checkpoint file, and close the window. You will be asked if you want to start the run immediately:



Choose **Okay** to start the calculation. The Gaussian 98W program will be started and a window will show the progress of the calculation, which should only take a couple of minutes. Wait until prompts have been given for the completion of all three calculations.

The results of the calculation are written to a text file with the name of your input file and a **.LOG** extension. You should save both the input and the output files on a floppy disk (that you can buy from the stockroom). The output or log file is a long file that follows the geometry optimization and subsequent vibrational frequency calculation. Look for the chart with frequencies in the output file as shown below:

Screenshot images courtesy of Gaussian, Inc. Used with permission.

```

Harmonic frequencies (cm-1), IR intensities (KM/Mole),
Raman scattering activities (A4/AMU), Raman depolarization ratios,
reduced masses (AMU), force constants (mDyne/A) and normal coordinates:

```

	1	2	3
	PIG	PIG	PIU
Frequencies --	711.2515	711.2515	782.2685
Red. masses --	1.5701	1.5701	1.0848
Frc consts --	0.4680	0.4680	0.3911
IR Inten --	0.0000	0.0000	129.9314
Raman Activ --	0.0000	0.0000	0.0000
Depolar --	0.0000	0.0000	0.0000
	4	5	6
	PIU	SGG	SGU
Frequencies --	782.2685	2043.1236	3416.5404
Red. masses --	1.0848	3.8066	1.0848
Frc consts --	0.3911	9.3623	7.4607
IR Inten --	129.9314	0.0000	69.6778
Raman Activ --	0.0000	0.0000	0.0000
Depolar --	0.0000	0.0000	0.0000
	7		
	SGG		
Frequencies --	3522.6947		
Red. masses --	1.2302		
Frc consts --	8.9945		
IR Inten --	0.0000		
Raman Activ --	0.0000		

Figure 7 – Vibrational Frequencies in the Output File

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Each vibration is labeled with its symmetry (PIG = Π_g ; SGU = Σ_u ; etc.), the vibrational frequency in cm^{-1} , and other information. Use this information to compare to your experimental results.

Table. The IR calculated frequencies (DFT B3YLP/6-311G) *versus* the experimental frequencies (cm^{-1}) for acetylene and deuterated acetylenes:

C_2H_2		C_2HD		C_2D_2	
calc.	exp.	calc.	exp.	calc.	exp.