Neutron Training Course – Day 5 and 6 (4 March 2014 and 5 March 2014)
Instrument: TOSCA
Title: Molecular Spectroscopy – practicum.

TOSCA is an indirect geometry spectrometer optimised for the study of molecular vibrations in the solid state. http://www.isis.stfc.ac.uk/instruments/tosca/

During the practical lecture we will perform experimental measurement of the inelastic neutron scattering spectrum of toluene (C6H5-CH3) at the temperature of 10 K. In doing so we will follow the following procedure:

1. Prepare toluene sample.
2. Attach the sample to the centre stick and load it into the cryostat.
2. Record inelastic neutron scattering (INS) spectrum of toluene.

For further brief information about the INS see Neutron Training Course manual, chapter 2 'Inelastic Neutron Scattering' by S.M. Bennington and S.F. Parker.

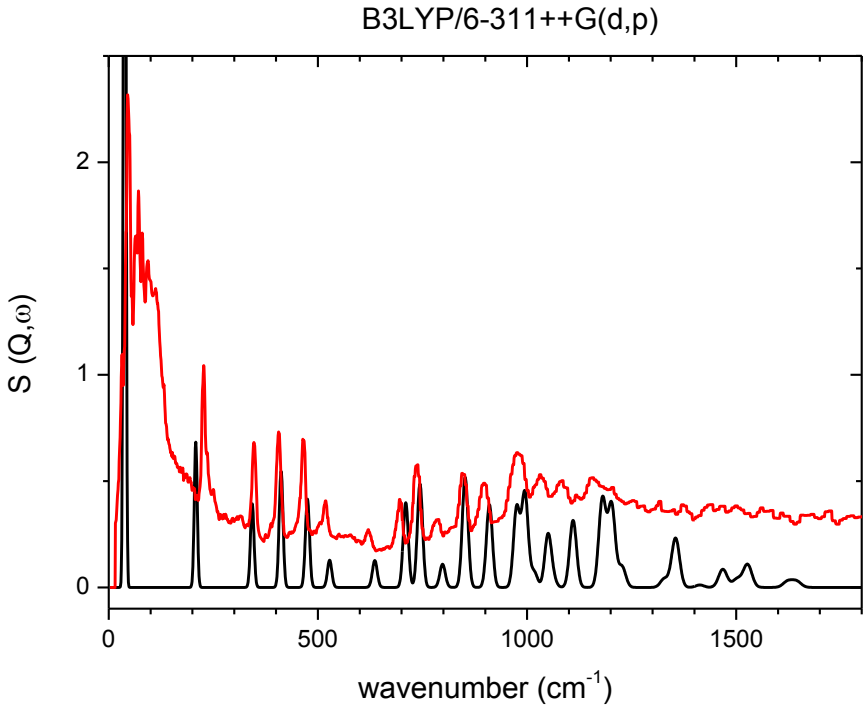


Figure 1. Inelastic neutron scattering spectrum of toluene recorded at 10 K (red trace). The black trace corresponds to the theoretical simulation of the INS spectrum at the B3LYP/6-311++G(d,p) level of theory.

Ab initio calculations were performed using the Gaussian 03 program and the resulting infrared spectrum was further utilized in association with a-CLIMAX software in order to derive INS spectrum.

In the second half of the practicum we will use GaussView and Gaussian 03 (Windows version) set of programs in order to perform ab initio calculations.

http://www.gaussian.com/g_prod/gv5b.htm
http://www.gaussian.com/

In doing so we will follow the following procedure:
3. Build up the molecule of interest using GaussView program.
4. Set-up Gaussian input file using GaussView program
5. Run the calculations and analyse the result of the calculations (both optimization and frequency part).

Question 1. Optimize the structure of CH_4 molecule and calculate vibrational frequencies at the following levels of theory:
(a) HF/6-31+G(d,p)
(b) HF/6-311++G(d,p)
(c) B3LYP/6-31+G(d,p)
(d) B3LYP/6-311++G(d,p)
(e) MP2/6-31+G(d,p)
(f) MP2/6-311++G(d,p)
What is length of the C-H bond in each case?
What is the frequency of the highest vibrational mode in each case?

	HF		B3LYP		MP2	
	R(C-H) / Å	Freq. / cm^{-1}	R(C-H) / Å	Freq. / cm^{-1}	R(C-H) / Å	Freq. / cm^{-1}
6-31+G(d,p)						
6-311++G(d,p)						

Question 2. Starting from the structure of CH_4 molecule optimized at the B3LYP/6-311++G(d,p) level of theory, perform a series of vibrational frequency calculations while varying the length of a single C-H bond. Write down the energy of the molecule as well as the frequency of the highest vibrational mode in each case.

R(C-H) / Å	Energy / A.U.	Freq. / cm^{-1}
1.00		
1.02		
1.04		
1.06		
1.08		
1.10		
1.12		
1.14		
1.16		

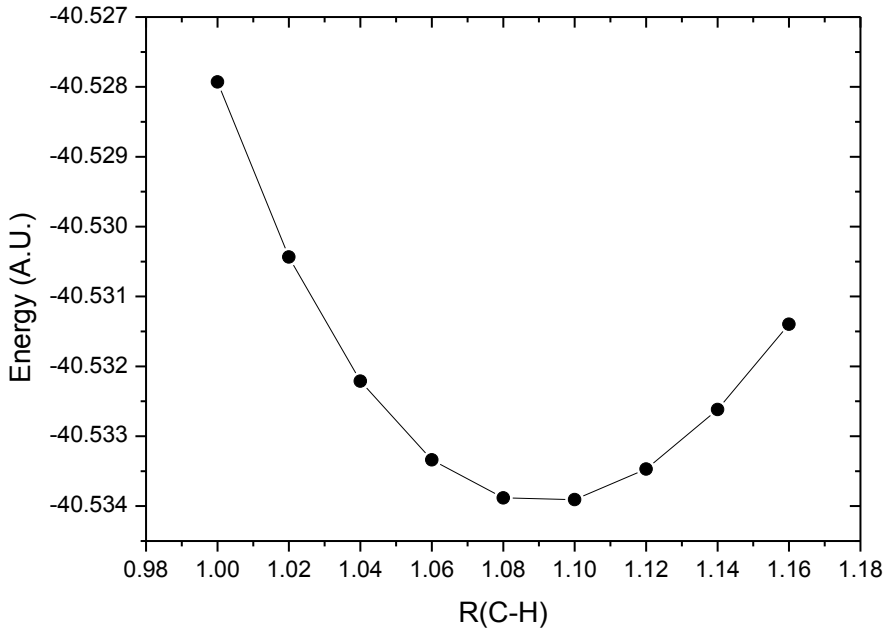
Question 3. Optimize the structure of C_6H_5-CH_3 molecule and calculate vibrational frequencies at the following levels of theory:
(a) HF/6-31+G(d,p)
(b) B3LYP/6-311++G(d,p)
(c) With the help of a-Climax software simulate theoretical INS spectra.
http://www.isis.stfc.ac.uk/instruments/tosca/software/tosca-software4727.html

Answer 1:

	HF		B3LYP		MP2	
	R(C-H) / Å	Freq. / cm^{-1}	R(C-H) / Å	Freq. / cm^{-1}	R(C-H) / Å	Freq. / cm^{-1}
6-31+G(d,p)	1.08386	3276.50	1.09272	3150.51	1.08688	3258.85
6-311++G(d,p)	1.08435	3252.23	1.09064	3132.07	1.09059	3207.82

Answer 2:

R(C-H) / Å	Energy / A.U.	Freq. / cm^{-1}
1.00	-40.5279287897	4014.3209
1.02	-40.5304339687	3797.2651
1.04	-40.5322115012	3591.0421
1.06	-40.5333384979	3396.4962
1.08	-40.5338832059	3215.6343
1.10	-40.5339080390	3132.4723
1.12	-40.5334690675	3133.3172
1.14	-40.5326169368	3134.1558
1.16	-40.5313974032	3134.9891



Answer 3:

(a) HF/6-31+G(d,p)

	Frequency/cm-1	IR intensity/ KM Mole^{-1}
1	14.4751	0.2437
2	227.8835	2.8828
3	367.2698	0.3858
4	453.8023	0.0042
5	519.2703	11.0884
6	561.3401	0.8331
7	679.5596	0.0742
8	771.2245	22.4740
9	819.7581	85.7226
10	848.5021	1.9073
11	952.0291	0.0267
12	1014.4381	1.1072
13	1077.3019	0.1189
14	1085.5754	0.0870
15	1103.5918	0.0010
16	1122.7952	0.0083
17	1124.2824	3.1485
18	1164.3467	6.3587
19	1177.9567	4.9847
20	1227.9244	0.1323
21	1292.8405	0.5718
22	1317.9672	0.4757
23	1339.9046	0.0029
24	1470.4129	0.0184
25	1546.4108	0.0175
26	1592.0858	0.0334
27	1613.2134	6.0460
28	1624.8411	13.7760
29	1658.9037	15.1081
30	1772.4060	0.8829
31	1799.4734	11.4874
32	3180.8834	38.6937
33	3238.3858	27.2673
34	3260.6189	24.3701
35	3331.8547	8.9322
36	3334.7266	5.1097
37	3347.5082	11.5527
38	3356.8625	47.2727
39	3369.8973	16.7711

(b) B3LYP/6-311++G(d,p)

	Frequency/cm-1	IR intensity/ KM Mole^{-1}
1	38.6926	0.2469
2	208.5515	2.3610
3	343.4879	0.3769
4	412.5829	0.0070
5	475.3215	9.8747
6	528.6646	0.5898
7	636.7566	0.0980
8	710.7177	31.9613
9	744.7177	49.1658
10	798.2271	0.8364
11	852.7386	0.0262
12	910.0931	0.6814
13	975.6035	0.0008
14	994.0086	0.0543
15	999.6821	0.1560
16	1017.1631	0.0781
17	1050.3167	3.7228
18	1062.9358	8.2736
19	1110.1679	6.2962
20	1180.8943	0.0536
21	1202.9526	0.4443
22	1227.7951	1.0151
23	1328.4487	0.0413
24	1355.6884	0.0015
25	1414.0372	1.1886
26	1468.2515	0.0071
27	1490.1413	7.2681
28	1502.3100	13.2878
29	1527.3037	13.5967
30	1623.2730	0.2526
31	1644.8336	9.1042
32	3019.5352	29.2597
33	3073.2906	19.5755
34	3099.2344	16.7530
35	3152.9586	8.7263
36	3154.6079	5.8111
37	3167.1956	7.2152
38	3175.4474	36.0373
39	3187.9865	14.0087

(c) See Figure 1.