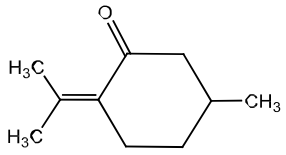
# Using WebMO and Gaussian to Predict Infrared and NMR Spectra: Pulegone

**Practical quantum theory background.** Recent advances in computing hardware and computational chemistry software have put powerful predictive tools into the hands of today's chemist. The original development of the quantum theory of atoms in the '20's by Erwin Schrödinger and others gave us the Schrödinger equation $H\Psi=E\Psi$ that may be considered the "Oracle of Chemistry." This equation tells the energy of electrons as they occupy different orbitals around the nucleus of an atom, or around multiple nuclei of a molecule. Exact solutions are not possible for large atoms or molecules, but various approximations have been developed that rely on rapid computation of integrals. One such approach is the **Hartree-Fock (HF)** theory of molecules which assumes that molecular orbitals (MOs) are formed by linear combination of atomic orbitals (AOs) on the constituent atoms.

It turns out that MO energies are more accurate if more AOs are used. That is, the larger the "**basis set**", the greater the accuracy of the results. The downside of using a larger basis set is the longer calculation time that is required. Many different basis sets have been developed; several of the most common are shown below along with the total number of basis functions, or AOs, for pulegone $C_{10}H_{16}O$. The basis sets in the table are "Pople" basis sets, which are named after John Pople a theoretical chemist who received the 1998 Nobel Prize.

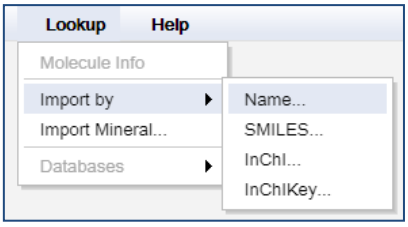



| Basis set | # Basis functions | Energy Calculation (min)* |
|---|---|---|
| 3-21G | 131 | 0.12 |
| 6-31G(d) | 197 | 0.25 |
| 6-31+G(d,p) | 289 | 0.70 |
| 6-311++G(2d,2p) | 457 | 2.7 |
| *B3LYP method; Gaussian 16; Antec12 compute node; cores = 2; wall clock time | | |

Hartree-Fock theory has been mostly superseded in practice by **density functional theory (DFT).** This approach uses the same basis sets, and places electrons in molecular orbitals. However, DFT also uses the important fact that if you know the total electron density, that is, the distribution of the molecule's electrons in space, then that uniquely determines $\Psi$. This was proved by Walter Kohn, who shared the Nobel prize with Pople, and Pierre Hohenberg. The exact mathematical relationship between density and $\Psi$ has never been identified, therefore many approximate methods have arisen. Historically, the most popular is **B3LYP**. Finding new and better DFT methods is an active area of research today. DFT is a little slower than HF theory, but it is more accurate.

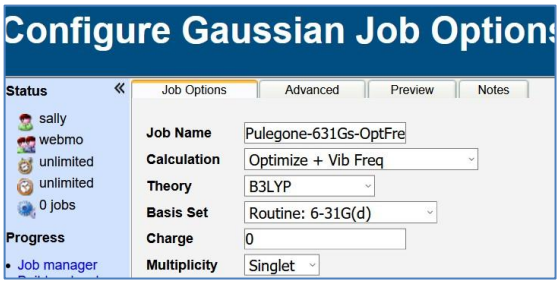
**Geometry optimization.** Exact VSEPR geometries are observed only in small symmetric molecules such as $CH_4$, $CCl_4$, $BH_3$, etc. In less symmetric molecules the geometry may be determined experimentally by x-ray diffraction. Or, geometry can be estimated computationally by geometry optimization, which involves iteratively changing bond distances and angles to minimize the molecule's total energy. This may require 10 to 50 steps alternating geometry changes and energy calculations. Gaussian does this automatically when the "opt" keyword is included in the input file. It is important to use the optimized geometry for predicting IR and NMR spectra, because only the optimum structure has a finite lifetime. A **non-optimum** (or non-minimum) structure is easy to detect: its vibrational spectrum contains one or more negative frequencies. These are "imaginary" frequencies, which are various motions having a zero restoring force. Note that some molecules may have two or more minimum-energy geometries: these are isomers.

**Step 1:** Log into WebMO. In the New Job menu choose Create New Job. Build or import the structure. To **build the structure,** left-click with mouse to add heavy atoms, and click-and-drag to create a bond. To make a double bond, click-and-drag twice. To add different atoms, use the periodic table icon in the left-hand margin. Click Cleanup, Comprehensive- Idealized: H's are added and the bond distances and angles are set to nominal values. **To import a structure**, do Lookup, Import by, Name. Type the name, "pulegone" in this case. Now click OK, then the right arrow at bottom of the screen. ➤ (Continue)



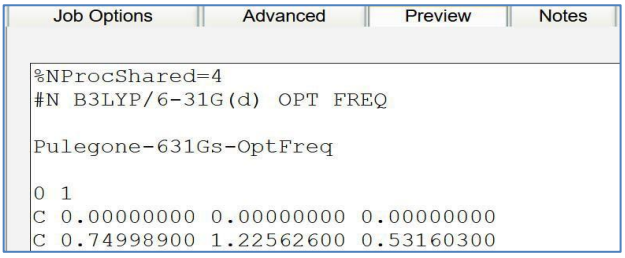

**Step 2: Choose Computational Engine.** Choose Gaussian. The **Select Server** box will read "First Available". This is the default, but may also select a specific server as seen in the drop-down menu. With the default setting, jobs are sent to the top of the list (currently Antec12 but this may change); if that one is busy, the job goes to the next one down the list, and so on. Click ➤

**Step 3: Configure Gaussian Job**. **Job Options** tab. Fill in a **Job Name**. Include some useful information. The **Calculation** pull-down reads Energy, Optimization, Vibrations, Opt and Vib, NMR and others. It is important to run a Vibration calculation after optimizing (to verify the lack of imaginary frequencies), hence "Opt + Vib" is often requested. The **Theory** pull-down reads HF, B3LYP, or others. Choose B3LYP. Under **Basis Set,** various Pople basis sets and others are shown; choose 6-31G(d). The **Charge** of a molecule is zero (pulegone is not an ion), and like most stable organic molecules, Multiplicity = 1; that is, all the valence electrons are paired. **Do not** click ➤ !

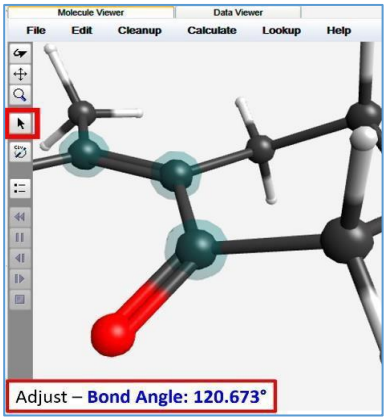



**Advanced** tab. Several vital settings, such as the number of **cores**, are controlled with the Cores box on this tab. Gaussian calculations are speeded up by using multiple cores of a multi-core processor. The default number is 4, however larger molecules will benefit from using 8, 12 or 16.

Click the **Preview** tab and **Generate** button. This shows the actual Gaussian input file created by WebMO for input. Keywords can be changed, added, or removed at this point. For example, if you decide to use 8 cores rather than 4, change the %NprocShared value accordingly. If you decide to do a more accurate calculation, change "6-31G(d)" to say 6-31G(d,p) or 6-31+G(d,p). **Now** click ➤….




**Step 4: Check Your Results. …**and you will be taken back to the **Job Manager**. You will see your job near the top of the list: the Status column will read Queued, then Running. At any time, you can check the progress of the calculation by clicking the magnifying glass icon under the Actions column at the right. After a few minutes (or hours, depending on the job), the Status column will read Complete. Click the magnifying glass icon or the job name to see the **Results**. The total energy is in the Overview section. Check the geometry using the Adjust tool (4th from the top). Click atoms (2 for bond length; 3 for bond angle; 4 for torsion angle) to display the values on the status line. The table of Vibrational Modes is near the bottom of the Results page. To view the IR Spectrum, set Peak Width to say 5 $cm^{-1}$ and click the icon. See Fig. 1. Animate a vibration by clicking the film icon in the table, or the peak in the spectrum. To stop the animation, click Reset View.



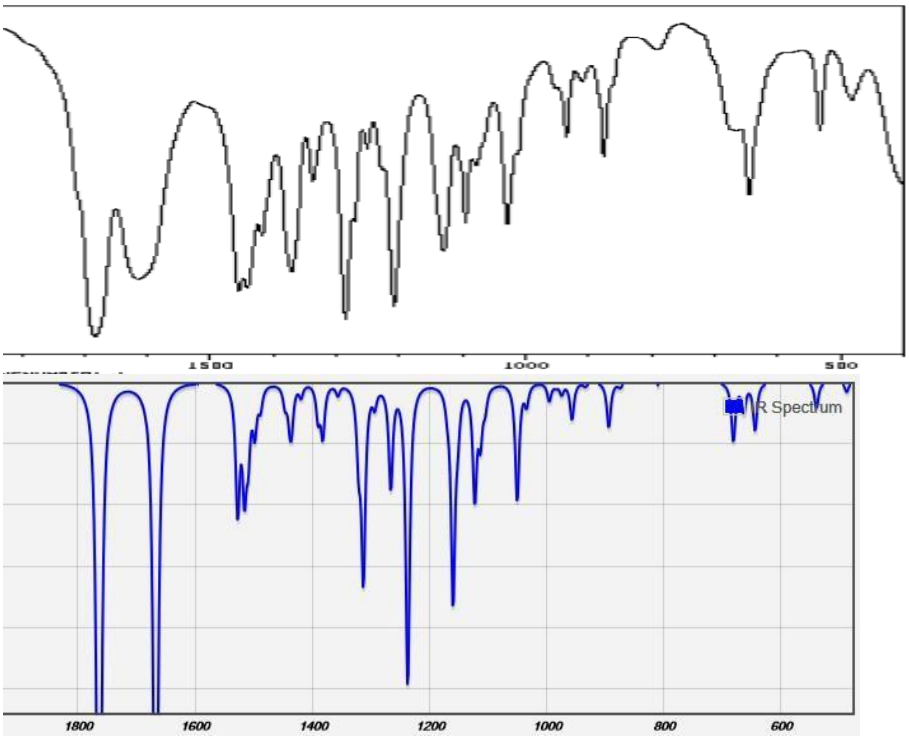
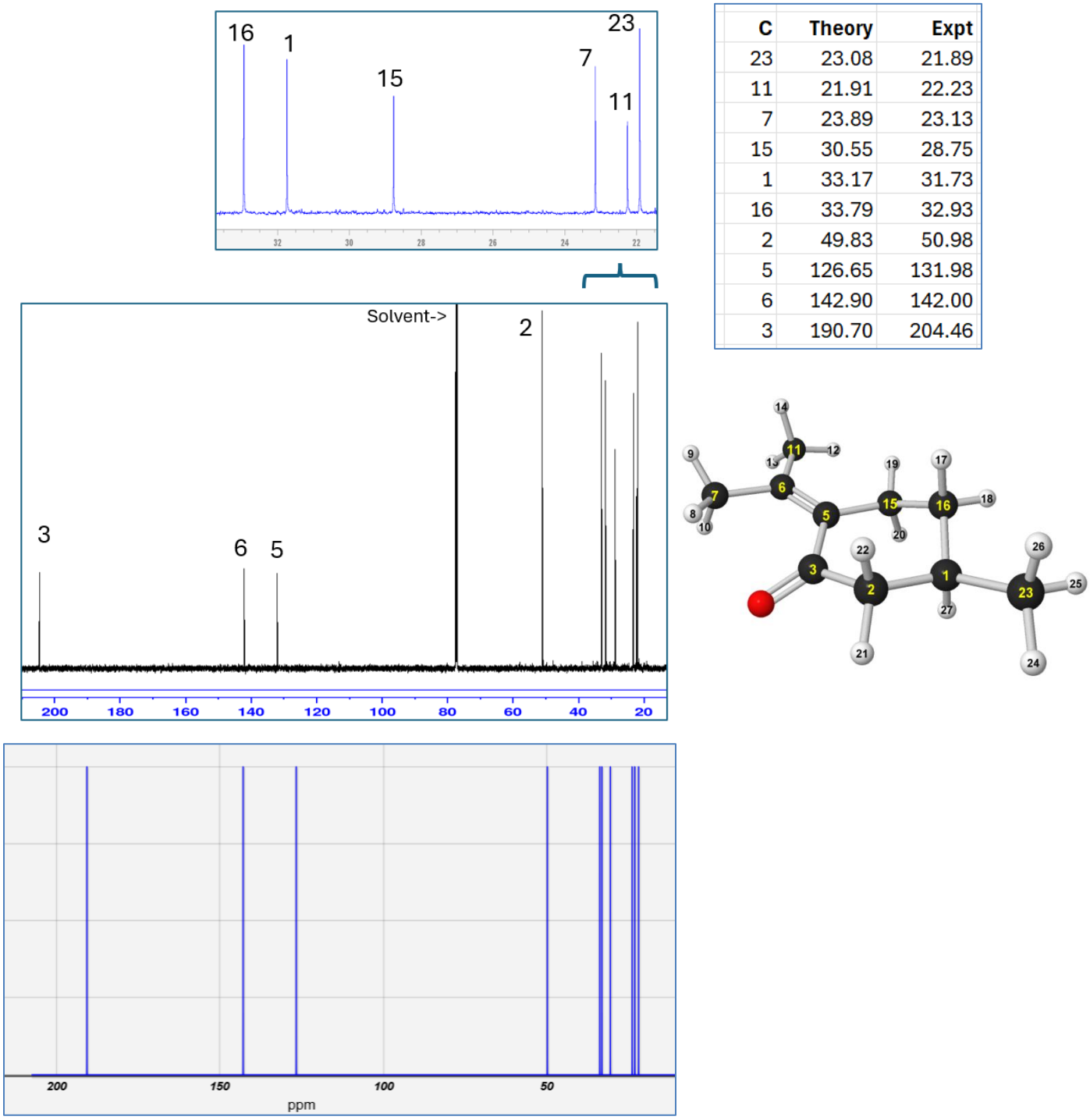


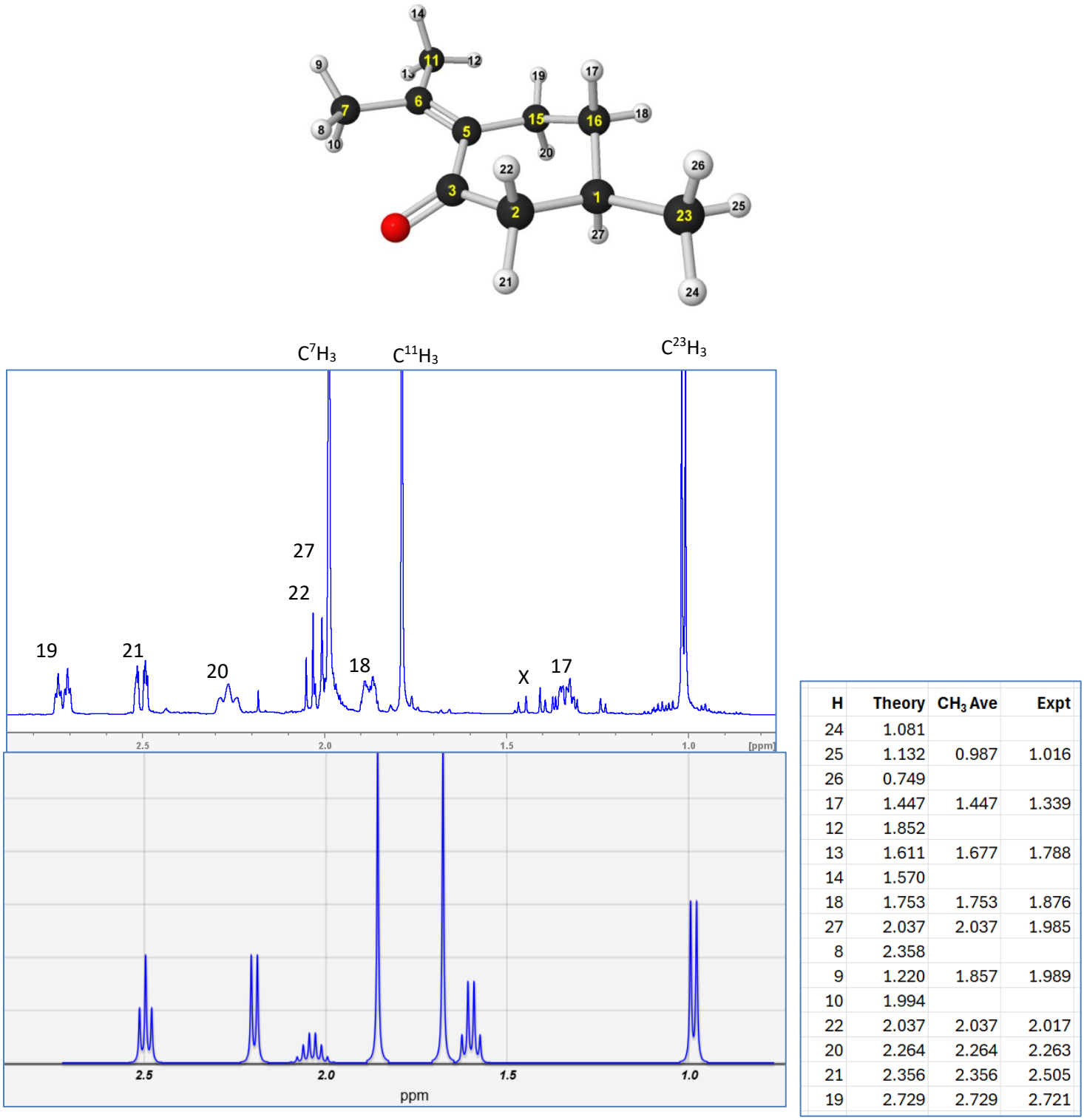

**Fig. 1.** Alignment of the fingerprint region of the experimental IR spectrum of pulegone (neat; from the Japan Spectral Database) with the B3LYP/6-31G(d) calculated spectrum: 15 to 20 peaks are assignable.

**Step 5: NMR (see pp 4 and 5).** Open the optimization job and click New Job Using This Geometry. Click ➢, choose Gaussian, First Available; then under Calculation, choose NMR. Use the same Theory and Basis Set. Click➢. When the job is Complete, open it. Near the bottom, enter TMS shielding values of 189.59 (C) and 32.18 (H). To see a spectral plot, click the magnifying glass icon. The results are summarized in Fig. 2 and Fig. 3. The C-13 spectrum looks much like a typical proton-decoupled spectrum. However, the H-1 spectrum looks different because WebMO has averaged $CH_2$ and $CH_3$ groups (check "Simulate proton splitting"), but the shifts of some non-equivalent H's are lost.




| C | Theory | Expt |
|---|---|---|
| 23 | 23.08 | 21.89 |
| 11 | 21.91 | 22.23 |
| 7 | 23.89 | 23.13 |
| 15 | 30.55 | 28.75 |
| 1 | 33.17 | 31.73 |
| 16 | 33.79 | 32.93 |
| 2 | 49.83 | 50.98 |
| 5 | 126.65 | 131.98 |
| 6 | 142.90 | 142.00 |
| 3 | 190.70 | 204.46 |

**Fig. 2.** Alignment of experimental (600 MHz, $CDCl_3$) (upper) and calculated (B3LYP/6-31G(d)) (lower) C-13 NMR spectra of pulegone.




| H | Theory | $CH_3$ Ave | Expt |
|---|---|---|---|
| 24 | 1.081 | | |
| 25 | 1.132 | 0.987 | 1.016 |
| 26 | 0.749 | | |
| 17 | 1.447 | 1.447 | 1.339 |
| 12 | 1.852 | | |
| 13 | 1.611 | 1.677 | 1.788 |
| 14 | 1.570 | | |
| 18 | 1.753 | 1.753 | 1.876 |
| 27 | 2.037 | 2.037 | 1.985 |
| 8 | 2.358 | | |
| 9 | 1.220 | 1.857 | 1.989 |
| 10 | 1.994 | | |
| 22 | 2.037 | 2.037 | 2.017 |
| 20 | 2.264 | 2.264 | 2.263 |
| 21 | 2.356 | 2.356 | 2.505 |
| 19 | 2.729 | 2.729 | 2.721 |

**Fig. 3.** Alignment of 600 MHz H-1 NMR spectrum of pulegone in CDCl3 (X = impurity) with the calculated (B3LYP/6-31G(d)) spectrum (below). Chemical shifts are listed at the right. In the calculated spectrum shown here both methyl and methylene peaks are averaged since "Simulate proton splitting" was checked in WebMO.