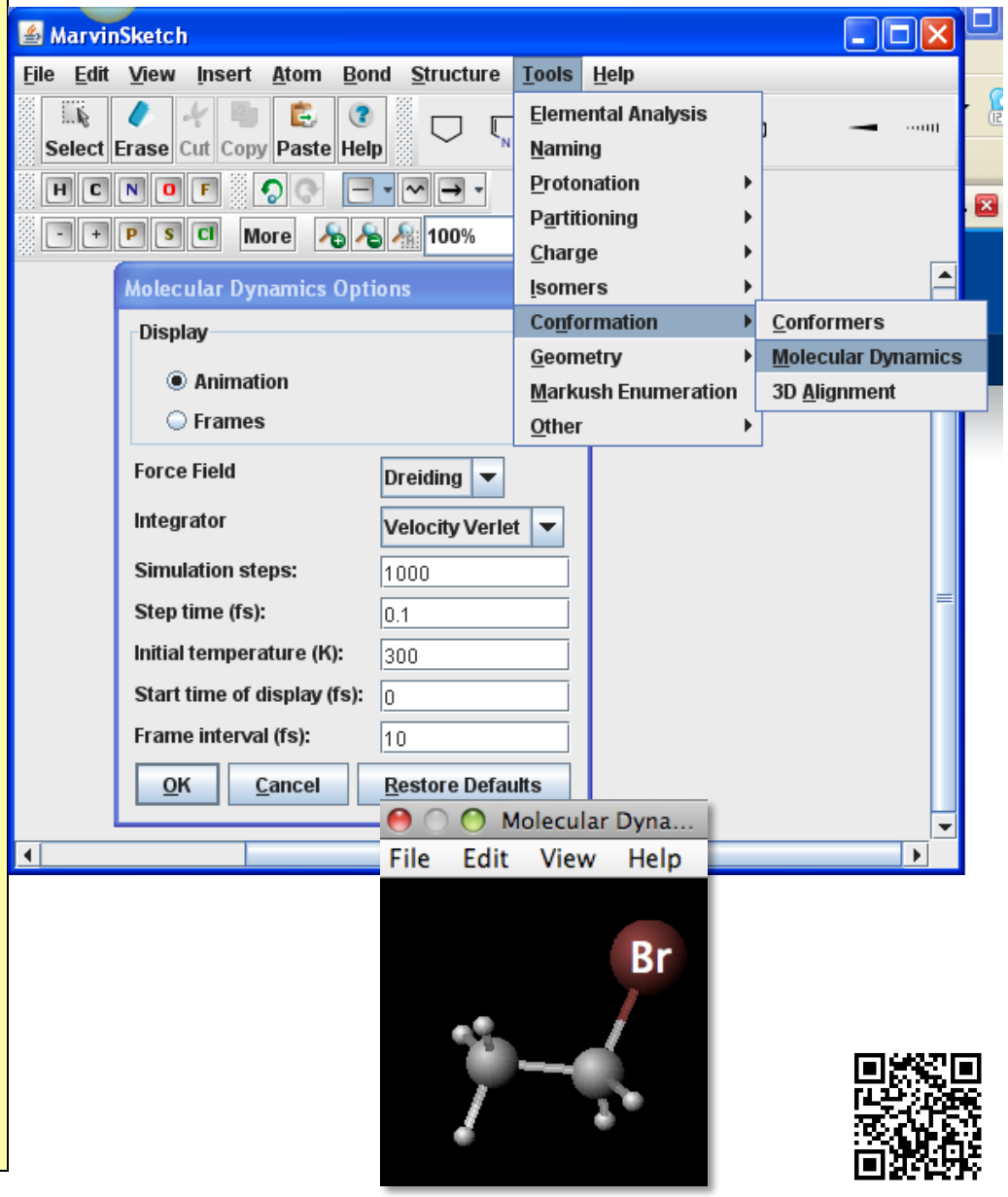
Atoms in Molecules are in Motion

At room temperature, molecules exhibit a lot of internal motion. MarvinSketch has a nice tool that simulates this dynamic character of molecules. Open MarvinSketch, draw EtBr (http://butane.chem.uiuc.edu/jsmoore/marvin_scripts/MarvinSketch_Practice.html). Call up "Molecular Dynamics" under "Conformation" in the "Tools" menu (see screen shot). Select the defaults; if necessary, set the "Simulation steps" to 10000 (not 1000). After clicking "OK", you'll need to be patient for a minute or so while your computer performs the calculation. In time, a new window will appear and an animation will be seen. You should notice that the light hydrogen atoms bounce around with high frequency, while the heavy bromine acts like a lead weight. The carbon atoms also experience rapid oscillatory motion. The animation represents 10000 steps spaced apart by 0.1 femtosecond (i.e., a fs is $1x10^{-15}$ sec). The total length of the simulation is approximately 1000 fs or one picosecond. A fs is not easy to comprehend, but a useful comparison is that a femtosecond is to a second, what a second is to a hundred million years. **Atoms in molecules are on the move!**

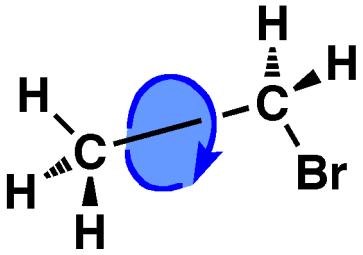


Dissecting Molecular Motion:

Rotation About Single Bonds

If you carefully observed the molecular dynamics simulation, you mostly noticed a lot of vibrations. Watch again and notice that the $-CH_3$ group oscillates like a torsion pendulum. If we could observe this simulation for a much longer time, we'd see rare instances in which the methyl group spins through the force that constrains it – i.e., on rare occasion the methyl group would appear to rotate rather than simply oscillate. Rotation about single bonds generates a different spatial arrangement of the atoms known as a **conformational isomer** (also called **conformer**, or **conformation**). The circular arrow in the diagram illustrates the type of twisting molecular motion known as **torsional rotation** that generates new conformation. The methyl group atoms ($-CH_3$) are fixed relative to the group in back which twists about the C-C bond axis. The angle of rotation is called the **dihedral** or **torsion angle**.

Conformational isomerism is a 3D aspect of molecular structure. Representations of conformational change must faithfully portray the 3D character of the molecule. Three ways of representing conformational isomerism are illustrated on the following slide. In each case, one of the carbon atoms and each of its three substitutents twist by an angle of 60˚. In the **perspective formula** the lines of normal weight are in the plane of the page, while the dash and bold lines are into and out of the page, respectively. The rotational trajectory of one of the hydrogen atoms is indicated in this figure. The bromine and other hydrogen atoms trace a similar trajectory. Carefully note the new locations of these atoms following rotation. The **sawhorse projection** attempts to show this same movement by projecting one carbon in front of the other, by angling the carbon-carbon bond that undergoes the rotation. You'll notice that the letter "C" representing the carbon atom has been left out for clarity. The location of this atom is at the point where the hydrogen atoms meet. The **Newman projection** is a view looking down the bond that undergoes the rotation. The carbon in front covers a portion of the C-H bonds in the back. This view clearly shows how the C-H bonds on one carbon are aligned relative to the bonds on the other.



Torsional rotation