Motivated by the experiments of Dexheimer et al. and Fleischer et al., we have performed simulations of the response of a C\textsubscript{60} molecule subjected to 12 fs laser pulses with fluences ranging from 0.07 to 4.40 kJ/m\textsuperscript{2}. We observe a symmetric excitation of electrons which softens the intramolecular bonding. As a result, there is a vibrational excitation which is almost purely in the breathing mode at low temperature. At the highest fluence, the vibrational amplitude is very large, with the diameter of the molecule oscillating between about 7.2 and 8.8 Å.

During the past few years, vibrational excitation\textsuperscript{1,2} and photofragmentation\textsuperscript{3,4,5} have been observed for C\textsubscript{60} molecules subjected to laser pulses with durations as short as 12 femtoseconds. Motivated by these experiments, and by potential applications to the photochemistry of fullerenes, we have performed simulations at both moderate and high fluences. We have also studied collisions of atoms with C\textsubscript{60} molecules following such ultrashort and ultra-intense pulses, to consider the possibility of laser-promoted encapsulation. In the present paper, however, we focus on vibrational excitation.

Details of the calculation will be given in a longer article. Here we mention only that the technique is tight-binding electron-ion dynamics\textsuperscript{6,7} and that the tight-binding model is that of Xu et al.\textsuperscript{8}

The results for several different fluences at two different temperatures are shown in Figs. 1-4. The first simulation, depicted in Fig. 1, is for a fluence of 0.07 kJ/m\textsuperscript{2}. The temperature T was chosen to be 0 K, so that the effect of this lower fluence laser pulse would not be intermingled with the effects of thermal vibrations. One can see that there is a sharp peak near 500 cm\textsuperscript{−1}, a frequency which is in very good agreement with the experimental value for the breathing mode of C\textsubscript{60}. Furthermore, a computer animation of the motion in real space and time shows that the response of the molecule to the laser pulse is indeed a symmetric breathing motion.

Analysis of the results shows that the electrons undergo a symmetric promotion from bonding to antibonding molecular states. It is the consequent bond softening which then leads to vibrational excitation.

Figure 2 shows the response at 300 K to a more intense pulse. Although the spectrum is complicated by thermal vibrations, the most prominent peak is again associated with the breathing mode. A comparison with the power
spectrum before the pulse (not shown here) demonstrates that the dominant new strength comes from this mode.

Figure 3 shows the response to a still more intense pulse. Despite the thermal vibrations, it is clear that it is again the breathing mode which is primarily excited. Notice however, that the frequency is shifted due to anharmonic effects, which result from the large amplitude of the vibrations. It is also clear that the response of the electrons is quite nonlinear. I.e., the electronic excitations involve multiphoton processes.

Finally, Fig. 4 shows the remarkably large amplitude vibrations whose Fourier spectrum is given by Fig. 3. The unusual behavior beyond 400 fs is a precursor of fragmentation. It should be mentioned that we have observed more rapid photofragmentation at still higher fluences, with emission of C$_2$ dimers, and these results will be reported elsewhere.

Acknowledgements

This work was supported by the Robert A. Welch Foundation.

References

Figure 1: Fourier power spectrum for a 12 fs pulse with a fluence of 0.07 kJoule/m² at T=0.

Figure 2: Spectrum for a 12 fs pulse with a fluence of 1.10 kJoule/m² at T=300 K.
Figure 3: Spectrum for a 12 fs pulse with a fluence of 4.40 kJoule/m$^2$ and T=300 K.

Figure 4: Diameter of C$_{60}$ molecule versus time following a 12 fs laser pulse with a fluence of 4.40 kJoule/m$^2$ at T=300 K.