FTIR Spectroscopy and Density Functional Theory of Carbon Clusters

Mekena McGrew, Undergraduate Researcher, Texas Christian University

Density Functional Theory (DFT)

Density Functional Theory is used in the molecular physics lab to predict harmonic vibrational frequencies of molecular systems and their isotopomers. DFT approximates solutions to the Electronic and energetic Schrödinger wave equation:

$$H_{el}\Psi_j = E^{el}\ \Psi_j$$

Where H is the electronic, or nucleic, Hamiltonian, E is the energy, and Ψ is the ground state wave function of the system.

Using electronic densities $|\Psi*\Psi|$ can analyze the ground state wave function and determine all other electronic characteristics of a system. The ground state energy of a system can be found by iteratively solving the Kohn-Sham orbital equations, until the electron density becomes constant. This accounts for the electronic interactions of the system.

The rotational, vibrational, and translational frequencies of a molecular system can be calculated from the potential energy surface, the total Energy, in the nucleic Hamiltonian.

$$H_{nucl} = -\Sigma(1/2M_A\ )\nabla^2_A + E_{total}$$

Minimizing the PES can optimize the geometry of a system and from there the frequencies can be found. The harmonic vibrational frequencies are directly proportional to the second derivative of the PES.
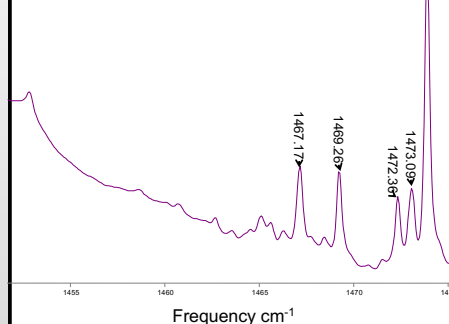
With the vibrational wave functions and electric dipole moment the infrared intensities can be calculated using a moment integral.

The DFT calculations can have a high error, so experimentation is needed to verify a molecules infrared vibrational frequency. These experiments are done using FTIR spectroscopy

Unknown Carbon Cluster 1474 cm^{-1} in the Infrared Spectrum
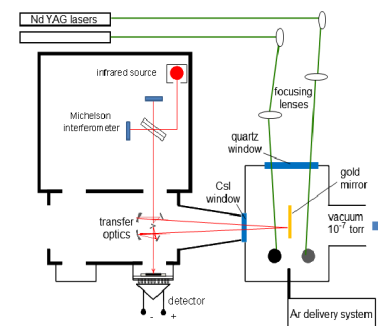
Res: 2 cm^{-1}

20% ^{13}C enriched rod

Frequency cm^{-1}

FTIR Experimental Setup: silicon-carbon dual ablation

FTIR Spectroscopy and Laser Ablation

Molecules are deposited onto a gold mirror, cooled to ~12K with a vacuum pressure of 1×10^{-7} Torr, by the ablation of rods using a Nd YAG laser. Argon in pumped through the system and creates a matrix around the molecules on the mirror. Argon is not detectable on the infrared spectrum is ideal to measure the spectra of molecules. After the deposition a spectra is ready to be taken.

Fourier Transform Infrared Spectroscopy (FTIR) detects and creates a spectra from the infrared light absorption and emission intensity of a sample at different wave lengths. A Fourier transform is calculated to the raw data (interferogram) into the spectra used to detect a molecular system.

Integrated Intensities, Ratios, and Equivalent Carbon Atoms

Infrared Frequency (cm^{-1})	Intensity	Ratio (shift/main)	Equivalent ^{13}C atoms (Ratio/20)
1473.9	0.0035707		
1473.1	0.001474	41.3	2.1
1472.3	0.0011488	32.2	1.6
1469.2	0.0013464	37.7	1.9
1467.2	0.0017544	49.1	2.5

By calculating the integrated intensities, intensity ratios, and probability we are able to obtain how many carbon atoms can be in the 1474 system. The table only shows the four most intense shifts because to measure the equivalent carbon atoms. It is thought a peak has symmetrical isotopomers, so in the theoretical systems symmetrical systems are used. It is hypothesized the system has 4 or 6 equivalent Carbon atoms, but further research is needed to be conclusive.

Potential Theoretical Molecular Systems

C_3 dimer
Vib frequency: 1477 cm^{-1}

C_4 rhombus
Vib frequency: 1398 cm^{-1}

Potential Carbon Clusters

C_4 bent
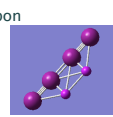
Polyacetylene
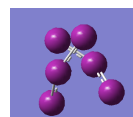
C_6 diamond

Conclusions

The ^{13}C shifts of the 1774 band had a small range, about 10 cm^{-1}. Molecules with smaller distances between atoms could have smaller ranges similar to the 1474 spectrum. Different functionals and basis sets for DFT theory could allow distance between atoms to be smaller, and could theoretically create the spectrum for the C_4 bent, C_6 diamond, and the Polyacetylene molecules.

The 1474 band could be a shift of an atom with greater intensity , or an unknown contaminate band. This is unlikely because the band is isolated and the nearest peak's ^{13}C are known.
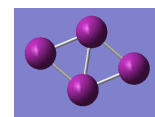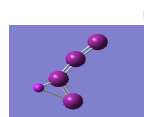
Acknowledgments