This research has involved the analysis and interpretation of spectroscopic data taken over a two year period from 1998 to 1999 at the Johnson Space Center. The data was taken in an attempt to perform diagnostic studies of the formation of carbon nanotubes in a laser produced plume. Carbon nanotubes hold great promise for the development of new materials with exciting properties. Current production processes are not sufficient to meet research and development needs. A better understanding of the chemical processes involved in carbon nanotube formation will suggest better production processes that would be more able to meet the demands of research and development.

Our work has focused on analysis of the emission spectra and laser induced fluorescent spectra of the carbon dimer, C₂, and the laser induced fluorescence spectra of the nickel atom, which is a necessary reagent in the formation of carbon nanotubes. Analysis of this data has given us information on rotational and electronic temperatures as well as lifetimes of these species during carbon nanotube formation in a laser produced plume. Results indicate that ablation of carbon and nickel and plume dynamics are strongly related to target temperature. Both the C₂ and Ni data show that an increased amount of material is ablated when the oven temperature, and therefore the target temperature, was increased from room temperature to 1473 K. The increase in ablated materials is seen not only in an increase in analyte signal but is also correlated with an increase in the detected distance of the plume’s propagation from the target surface and the detected lifetimes times of the species. The increase in lifetime of the emission signal from hot C₂ is on the order of hundreds of microseconds and the increased propagation distance is on the order of a few millimeters, with respect to the surface of the target. The changes for the lifetime of the nickel atom signal are more dramatic, the lifetime of the laser induced fluorescence signal changes from tens of microseconds to several milliseconds as a consequence of heating. The distance of the detected nickel atom from the target surface also increases with temperature, but not to the same extent as that of the C₂, consistent with a measured slower propagation rate for the nickel atom. The increase in ablated materials and distance of the plume propagated as a consequence of increased target temperature combine to created more nickel atoms and C₂ available for a longer time.
within the inner tube region of the production apparatus. Since an oven temperature of 1473 K is necessary to form a good yield of carbon nanotubes, it would seem to imply that the time required for carbon nanotube formation is, at the very least, some hundreds of microseconds to several milliseconds and that a high density of molecular species in a confined reaction region is required.

Though signal intensities and lifetimes change as a function of target temperature, the rotational temperatures of C₂ and the electronic temperature of the nickel atoms do not appear to change significantly as a function of target temperature. The nickel atoms exhibit an electronic temperature of at least 1,500 K at the peak of the signal intensity and cooler temperatures of approximately 300 K at lesser intensities for both a cold and a hot oven. Rotational temperatures of C₂, as obtained from laser induced fluorescence spectra, are lower than would be expected, ranging from about 400 to 700 K, based on an equilibrium temperature of 1473 K produced by the oven. Again, the more intense signals produce the higher rotational temperatures. It should be noted that emission temperatures for the C₂ species are on the order of several thousand Kelvin. It is clear that a thermal equilibrium does not exist within the plume. The lower than expected rotational temperatures for C₂ would imply that energy is lost to some other, yet to be identified process. This process may be a general nucleation process for carbon, or a process related to carbon nanotube formation.

The thermodynamic and kinetic information is important in the analysis of proposed mechanisms. Proposed mechanisms differ with respect to the kinetics, cluster sizes, and thermodynamics of the intermediate species involved in nanotube formation. Kinetic models predict nanotube formation times ranging from a few microseconds to several seconds. Though our experimental setup could not detect larger carbonaceous species and metal clusters, the density calculations based on signal intensities in correlation to the amount of materials ablated from the target would imply that a large percentage of the
carbonaceous material still exists as a dimer for at least a hundred microseconds and large percentage of the metal exists as an atom for milliseconds. This is in contrast to models that proproat large particle ablation or droplet ablation processes. It is still unclear how aggregation of metal and carbonaceous clusters is involved in the formation process for the nanotubes since we do not know the time at which the nanotubes are being formed. Metal atom clusters may become important to nanotube formation at times later than several milliseconds but less than several seconds. Additional efforts to isolate formation times for the nanotubes themselves would be highly complimentary to this work. This work has been submitted for publication to the Journal of Applied Physics and has been accepted with minor revisions. Revisions have been made and the manuscript has been resubmitted.

Though additional work to design experiments aimed at determining the presence of nanotubes within the laser produced plume would be very beneficial, it is unclear as to how such experiments might be designed in the immediate future. However, there is work that can be done immediately on data already obtained in various other experiments performed at NASA-JSC that would be complimentary to this and other previously reported work. One set of such data explores the emission spectra of the carbon dimer under various laser combinations of infrared and visible lasers, including the use of one, two, and three lasers. Analysis and interpretation of this work with respect to our previous work would be very helpful in further refining carbon nanotube formation models. This work will focus on the analysis of a, yet to be identified, broad, underlying absorption band that may be related to metal carbon dimer interactions, and the electronic, vibrational, and rotational temperatures of the carbon dimer as a function of laser combination and intensity. The spectroscopic information, along with characterization of the nanotube products, under the various laser conditions may give additional elucidation into the chemical mechanisms. This work will be explored under the new grant for 2000-2001.
In summary, the work performed at LeTourneau by faculty and students has provided an analysis of experimental data obtained at NASA-JSC. The analysis has allowed for the interpretation of various models proposed for carbon nanotube formation. Our analysis is consistent with a mechanism involving ablation of small carbonaceous species and atomic metal. The molecular and atomic species do not appear to be in thermodynamic equilibrium. Nanotube formation likely occurs upon aggregation of these small species some hundred microseconds to several seconds after ablation. These results have been compiled into a paper submitted to the Journal of Applied Physics. We hope to continue similar analytical work using data from other experiments. Interpretation of this analysis with respect to our previous work, and any other works by other groups published in the literature, will allow further refining of the chemical mechanisms involved in carbon nanotube formation. It is expected that such information would lead to more efficient production methods and enhancement of current methods that would better enable research and development in new materials incorporating carbon nanotubes.