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13. ABSTRACT (Maximum 200 words)

Two new types of infrared spectrometers have been developed for the study of gas-phase cluster species. A tunable far-infrared (FIR) laser was combined with an apparatus for producing planar supersonic beams of laser vaporized clusters, and used in the measurement of the 64.1 cm^{-1} bending vibration of C_3. A mid-IR diode laser system was constructed with a similar cluster source, and used in studies of the C_4, C_5, C_7, and C_9 clusters. Structures and internal dynamics of the clusters were determined. Extensions to metal cluster systems are currently underway.

A new type of spectrometer was developed for measuring electronic spectra of supersonic metal clusters. Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) was utilized in a study of the Cu_3 cluster in the initial application of the method.

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OFFICE OF NAVAL RESARCH

FINAL TECHNICAL REPORT

for

Contract #N00014-87-K-0270

"Structures, Properties, and Dynamics of Metal Clusters from Infrared Laser Spectroscopy"

In this research project, three new types of spectrometers were developed for the study of metal clusters. The idea was to address the central question of determining cluster geometry directly, by determining moments of inertia from rotationally-resolved spectra. Moreover, with such high resolution methods, the dynamics of clusters (e.g. pseudorotation, quasilinearity) could be probed in a rigorous fashion. No other existing experiments have the capability to carry out such measurements.

A tunable far-infrared (10-200 cm^{-1}) laser spectrometer was constructed (Refs. 7,8) for measuring the vibrational motions of metal clusters. The initial targets were Na_3 and Cu_3, both of which exhibit complex internal dynamics as a result of Jahn-Teller couplings. The system employs Schottky diode frequency mixing of a cw line-tunable FIR laser and a continuously tunable (2-120 GHz) microwave spectrometer for generation of FIR radiation. Clusters are made by excimer laser vaporization of a target in a planar supersonic expansion. Spectra are measured in direct absorption with a multipass design. The system was constructed and tested in a study of the C_3 cluster. The 63.1 cm^{-1} bending mode of this cluster was measured for the first time (Ref. 3). However, our first attempts to study Cu_3, Na_3, and Li_3 have not been successful, upon expiration of this grant.

A mid-IR laser spectrometer was constructed for the purpose of studying clusters with higher vibrational frequencies (Be_n, overtones, etc.). In this region, the available technology is more advanced, such that commercial diode lasers could be employed as the radiation sources. Clusters were generated in a similar way, employing an excimer laser. With this system, the carbon clusters C_4, C_5, C_7, and C_9 were investigated in detail (Refs. 2, 4, 5, 6). The structures and vibrational dynamics were characterized. The sensitivity of the spectrometer is now sufficient for addressing metal clusters. The first project is to be Be_4, which has accessible low-frequency vibrations. We are currently developing a chemically safe apparatus for working with this extremely hazardous element.

A new method for measuring electronic spectra of metal clusters in direct absorption was developed. In the technique (Cavity Ringdown Laser Absorption Spectroscopy), clusters are created in a supersonic expansion through laser vaporization. A pulsed dye laser generates a 10 usec pulse of light, which is injected into a high finesse optical cavity. Since the coherence length of the pulse is short relative to the cavity length, the pulse acts as a "particle" in the cavity, making many (~1000) passes before decaying exponentially through transmission and absorption. The transmission is monitored with a photomultiplier, which outputs a decaying exponential signal (the "cavity ringdown"). When a metal cluster pulse is injected into the cavity simultaneously with the laser pulse, the decay constant changes. By taking the log of the change, the absorption coefficient is measured for each individual laser shot. The absorption sensitivity is near 1 part in 10^6.

The technique was initially demonstrated on the Cu_3 cluster. The spectrum originally measured by Smalley using resonant multiphoton ionization spectroscopy was observed, showing new features that confirmed the existence of IVR in the upper state (Ref. 1). It appears that this new technique will be quite powerful for studying metal clusters in the very near future.

ONR Contract # N00014-87-K-0270

Publications - January 1, 1990 - December 31, 1990

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8. G.A. Blake, K.B. Laughlin, R.C. Cohen, K.L. Busarow, D-H. Gwo, C.A. Schmuttenmaer, D.W. Steyert, and R.J. Saykally, "The Berkeley Tunable Far Infrared Laser Spectrometers," Rev. Sci. Inst. (in press).