Co-axially Configured Supersonic Jet Spectrometer For Submillimeter Investigations of Non-covalent Interactions

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Abstract—**The current status in the development of a phase and frequency stabilized co-axially configured submillimeter supersonic jet spectrometer will be described. The performance characteristics of the spectrometer will be illustrated by investigations of non-covalent interactions including van der Waals and hydrogen bonded complexes.**

I. Introduction And Background

Since the initial application of submillimeter-wave backward wave oscillator (BWO) technology for spectroscopic purposes,[1] there has been significant interest in instrumental and associated technique developments for a range of applications.[2-6] In addition, pulsed-nozzle FT microwave spectroscopy has become recognized as a powerful method for characterizing the fundamental properties of non-covalent intermolecular interactions particularly structural[7]. A submillimeter spectrometer capable of similar versatility as well as relatively comparable resolution and sensitivity to the latter could also be effective. This particularly relates to enhancing investigations of such complexes into a higher frequency regime greatly enhancing their spectroscopic characterization. Recently, there have been efforts to develop a submillimeter-wave absorption spectrometer with a coaxially configured pulsed jet for enhancing spectroscopic characterization for such purposes[8]. Generation of data that is relevant to the determination of accurate semi-empirical potential energy surfaces of small triatomic van der Waals and tetra-atomic hydrogen bonded interactions especially those involving low frequency vibrations and the characterization of isomeric structures have been stressed. Such a co-axially configured spectrometer has been designed, developed and its current performance is now described. A critical evaluation of its characteristics and capabilities including ultimate precision, accuracy and resolution for spectroscopic applications to weakly bound complexes will be emphasized including incorporation of a discharge capability for vibrationally excited state studies. The potential application of the spectrometer to complexes with larger vibrational dimensionality will also be discussed.

A. RESULTS

A co-axially configured sub-mm wave supersonic jet spectrometer with a frequency and phase stabilized back-ward wave oscillator (BWO) has been developed and applied for the study of jet cooled molecules and dimers. The spectrometer has now been demonstrated to operate up to 800 GHz with both technical resolution and accuracy of frequency measurements of ~1 kHz. The hard and soft ware of the spectrometer permits rapid (3.5 μs /step) digital scan frequency of phase locked BWO in a range of 1 kHz to 20 MHz with a frequency step size of 10 Hz to 100 kHz. The initial performance of the spectrometer will be rigorously evaluated through spectroscopic investigations of the Ar-HBr complex and its isotopomers. Rovibrational molecular parameters for these isotopomers will be compared to ground state results from state-of-the-art pulsed-nozzle FT microwave spectroscopy and the technique demonstrated to provide rovibrational parameters of comparable accuracy. Investigations of the lowest Σ-bending vibrations of Ar-DBr(v=0) and Ar-HBr(v=1) will also be reported using the co-axially configured supersonic jet spectrometer, the latter using glow discharge excitation. Analyses of hyperfine substructure in these spectra provide accurate molecular parameters for Ar-DBr and Ar-BrD isomeric states, direct determination of their corresponding isomerization energies, and respective parameters in the v=1 HBr stretching vibration of the Ar-HBr isotopomer. This experimental data is used as a sensitive probe of the relative energies of potential minima for an accurate CCCC 3-D Ar-HBr morphed potential. Furthermore, investigations of the Ar-HI complex will be used to probe the intensity capabilities of the instrument and an investigation of the population distribution of this species in the supersonic jet expansions.

Futhermore, the spectrometer is used for precise measurements of a hyperfine structure resolved spectra of molecular complexes $(HBr)_2$, $(HI)_2$ and can be applied for detailed measurements that probe the intermolecular dynamics of these hydrogen bonded dimers.

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