

High Resolution Infrared Spectroscopy of Slit-Jet Cooled Transient Molecules:
From van der Waals Clusters, to Hydrogen Bound Dimers, to Small Organic
Radicals

by

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Radicals

Thesis directed by Adjoint Professor David J. Nesbitt

This dissertation describes high resolution ($< 0.0005 \text{ cm}^{-1}$), high sensitivity (absorbance sensitivity $\approx 2 \times 10^{-6}$ per root Hz), direct absorption, infrared laser spectroscopy of transient molecules formed in a slit supersonic expansion. A series of molecular species, ranging from weakly bound van der Waals clusters, through hydrogen bound dimers, to a group of small organic free radicals are investigated. The advantages provided by the combination of a high optical resolution and the rotational and translational cooling of a slit supersonic expansion are exploited to probe an array of spectroscopic and dynamic phenomena.

Investigations which probe the $v = 1 \leftarrow 0$ vibrational transition for the hydrogen halides DF and HCl sequentially clustered with one through three Ar atoms are presented. Vibrational redshifts and rotational constants are compared with theoretical calculations on accurate pairwise additive potentials, providing insight into the importance of many body terms. Near-ir spectroscopic investigations of the hydrogen bond prototype $(\text{HF})_2$ and its isotopomer $(\text{DF})_2$ are also presented. For both isotopomers, all four, large amplitude *intermolecular* vibrations are observed as combination bands built on top of intramolecular

excitation. In addition to vibrational energies, mode specific vibrational predissociation rates, interconversion tunneling rates, and rotational constants are reported. Comparison with full 6-D quantum calculations provide an unprecedented test of trial hydrogen bonding potential energy surfaces.

A novel high-intensity source of jet-cooled molecular radicals and ions is also described based on the combination of i) slit supersonic expansions with ii) electric discharges. Confinement of the discharge to a region just prior to supersonic expansion results in efficient rotational cooling of molecular radicals. Infrared studies of methyl, ethyl, allyl, and cyclopropyl are presented. Resolution of fine and hyperfine structure provides information about spin polarization effects in methyl radical. The first rotational assignment of ethyl radical is presented, providing information on hyperconjugation effects, and, coupled with a multidimensional quantum mechanical modelling, information about the large amplitude internal rotation and CH₂ bend. A spectral analysis of two vibrational bands in allyl is presented, as well as an analysis of spectral broadening due to spin rotation effects. Finally, the first spectroscopic detection of cyclopropyl radical is also presented.

DEDICATION

To Kim

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Graduate school has been a profound experience. I feel as if I am at the end of my own, personal epic journey. Over seven years ago I rode my motorcycle into Colorado with no idea of what I was actually beginning. Now I am at the end. Throughout this prolonged and sometimes tumultuous endeavor numerous people have impacted my life, adding richness, flavor, and often meaning to what otherwise might have been a large collection of lonely nights surrounded by impersonal lasers and electronic boxes. To all those people, I offer my deepest thanks.

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