

HIGH SENSITIVITY AND HIGH FREQUENCY ROTATIONAL SPECTROSCOPY

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With a newly designed and constructed high sensitivity intracavity millimeter-wave spectrometer operated with a pulsed supersonic jet, we have succeeded in detecting the pure rotational *b*-type transitions of various van der Waals complexes. Amongst them are Ne-CO, Ar-CO, N₂-CO. Very recently we detected millimeter wave transitions of the astrophysically relevant van der Waals complex CO-H₂. In the present contribution, we shortly outline the new intracavity spectrometer and we will discuss the general structure of the spectra of some van der Waals complexes. The sensitivity of the intracavity spectrometer was checked by recording the $J = 1 \leftarrow 0$ rotational transition of ¹³C¹⁷O near 107 GHz in natural abundance and has been found to be a factor of about 100 more sensitive than "conventional" millimeter wave jet spectrometers. The operational frequency range of the intracavity spectrometer covers the region from 107 to about 145 GHz.

The new millimeter-wave spectrometer combines two techniques, intracavity operation with low temperature molecular production in a supersonic jet. The molecular jet is placed into the cavity, in order to detect and measure with high accuracy extremely weak spectral lines of molecules or molecular complexes, which possess small dipole moments and/or exhibit low abundances.

The high resolution, broadband scanning spectroscopy with microwave accuracy has been extended into the terahertz region by using frequency and phase stabilization of continuously tunable backward wave oscillators (BWOs) at frequencies up to 1.25 THz. In combination with frequency multiplication techniques and laser sideband techniques, this BWO based method allows broadband scanning spectroscopy to be extended to 3 THz. Very high sensitivity and frequency resolution have been achieved. The spectral resolution has been pushed by saturation techniques into the sub-Doppler domain.

Some of the stable species such as CO, NH₃, HCl, and others have been investigated by saturation spectroscopy, resulting in line widths of < 40 kHz, well below the Doppler line widths, and in favourable cases with line center determinations of < 1 kHz at frequencies near 1 THz. Employing frequency multiplication techniques and laser sideband techniques with BWOs, high sensitivity spectroscopy near 2 THz has been achieved. For example, rotational transitions in vibrationally excited states of CO have been observed and measured to high accuracy around 2 THz. The recording of spectra of other molecules such as HSSH is in progress.

MOLECULAR SYMMETRY AND SPECTROSCOPY: THE SECOND EDITION

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The first edition of *Molecular Symmetry and Spectroscopy* by P. R. Bunker was published by Academic Press in 1979. We have now written The Second Edition. It is to be published by The National Research Council of Canada Research Press (<http://www.nrc.ca/cisti/journals/mgraphs.html>), and it will be available in late 1998. To reflect the very significant progress that has been made in high resolution molecular spectroscopy over the last 20 years it has been necessary to increase greatly the amount of material covered, and the new edition is about 50% longer than the first edition. As before the central theme is the use of symmetry in the understanding of molecules and molecular spectra, with emphasis on the use of the molecular symmetry group. The presentation of the material has been altered so that the molecular symmetry group is introduced early on (in Chapter 3). Many experimental spectra are displayed to illustrate the theory. This talk will review the contents of the book.

MAGNETIC VIBRATIONAL CIRCULAR DICHROISM - AN ALTERNATIVE METHOD FOR DETERMINING MOLECULAR ZEEMAN G-VALUES. SIMULATIONS AND MEASUREMENTS ON EXAMPLE SYSTEMS

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Molecular Zeeman spectra of small symmetric molecules have been measured directly for at least two decades using various high resolution techniques, primarily focussed on rotational properties of the ground state. We have now measured a number of molecular Zeeman g-values using a relatively modest resolution tool (0.1 cm⁻¹ with an FTIR) by taking advantage of the frequency to intensity conversion possible via magnetic vibrational circular dichroism (MVCD) used as a detection method for the magnetic field perturbation. Spectra of diatomics and symmetric top molecules like HCl, CO and NH₃ can be fully simulated with a conventional Hamiltonian. Unlike microwave based spectroscopies, MVCD measures properties of excited vibrational states. In most cases studied to date, these closely reflect the ground state rotational g-values, implying little structural change in the excited state. In a few cases, notably the C-H bending modes of acetylene and methane, distinct vibrational Zeeman effects were detected. For acetylene these have been simulated with a Hamiltonian and a vibrational g-value has been determined and compared favorably to predicted values derived from the paramagnetic susceptibility as computed quantum chemically.

ADVANCES IN STARK EFFECT MEASUREMENTS IN A MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROMETER

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In a molecular beam Fourier transform microwave spectrometer (FTMW) a static electric field can be applied to two square-shaped electrodes. The presence of the external field induces a frequency shift and split of the rotational lines. Among others, one of the outstanding applications of Stark effect measurements was the determination of the dipole moment of the water dimer¹.

For the first time Stark experiments in a FTMW spectrometer are successfully performed with the pulsed molecular beam coaxial to the resonator axis, together with a new geometry for the Stark electrodes which prevents from line broadening due to E-field inhomogeneity². Our new configuration provides a considerable improvement in resolution and sensitivity in comparison to the commonly used arrangement for dipole moment determination with a FTMW spectrometer, with the molecular beam perpendicular to the resonator axis³. The linewidth achieved is now close to the typical value found in absence of a Stark field⁴, less than 10 kHz at 10 GHz, HWHH, which makes the system optimal for yielding precise information on structure and charge distribution of molecular complexes.

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COBRA - FOURIER TRANSFORM MICROWAVE SPECTROSCOPY: LARGE MOLECULES OF ASTROPHYSICAL INTEREST IN THE LABORATORY

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Since their first observation in the thirties the so-called 'Diffuse Interstellar Bands' (DIBs) could not be attributed to a single carrier or class of carriers. Nevertheless, a quite large number of potential candidates were proposed: Polycyclic aromatic hydrocarbons (PAHs), interstellar grains, fullerenes, long carbon chains and even microorganisms.

In our experiment, a 'Coaxially Oriented Beam-Resonator Arrangement' Fourier transform microwave (COBRA-FTMW) spectrometer, long carbon chain type molecules are produced in a DC-discharge nozzle and immediately expanded as a pulsed supersonic jet into a Fabry-Perot type resonator.

We will present our newly developed cryogenic COBRA-FTMW spectrometer^a and a number of carbon chain type molecules that have been discovered for the first time with this apparatus. Among those are polyynes, free radicals and carbenes with up to 19 atoms^b.

^aJens-Uwe Grabow, E. Samuel Palmer, Michael C. McCarthy, and Patrick Thaddeus, to be published

^bWei Chen, Carl A. Gottlieb, Jens-Uwe Grabow, Michael C. McCarthy, Michaeleen R. Munrow, Steward E. Novick, Michael J. Travers, and Patrick Thaddeus, submitted