

# FAR-INFRARED LASER STARK SPECTROSCOPY OF CD<sub>3</sub>OD: DETERMINATION OF THE ELECTRIC DIPOLE MOMENT

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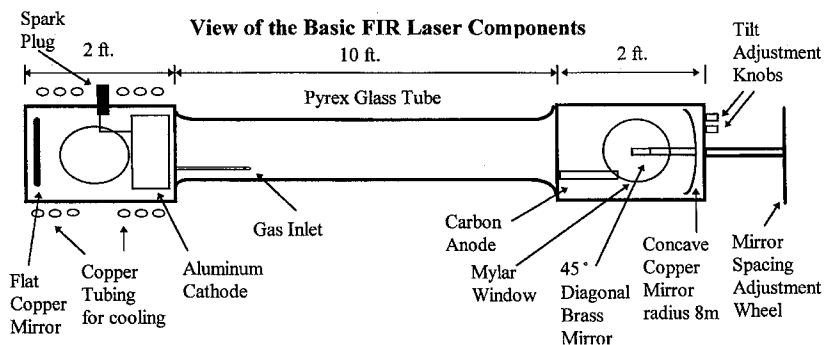
Far infrared (FIR) laser Stark spectra of CD<sub>3</sub>OD were recorded using a direct discharge molecular gas laser, operating with HCN as the lasing medium at 311  $\mu\text{m}$ . Recently, Fourier transform far infrared (FTFIR) spectra was recorded in Giessen Germany for this molecule. By combining the results of the Stark spectra with the results of the FTFIR spectra the  $\gamma\text{m}$  component of the electric dipole moment for this species of methanol was determined for the first time.

In deciphering the structure of matter, optical spectroscopy has been the greatest tool available to the scientific community. For instance, electron spin, nuclear spin and nuclear magnetic moment can all attribute their discoveries to spectroscopy. Thus far, the majority of information available about molecular structure and dipole moments has been provided mainly through microwave spectroscopy. Our spectroscopic investigations are carried out in the FIR region, which spans from 0.01 mm to 1 mm. This region is difficult to explore experimentally, hence there is a need for specialized techniques. The information obtained through spectroscopy in this region is of significant importance to further research. This is especially true of methanol and its isotopes. One reason the study of methanol and its isotopes is important is because they are the simplest molecules to exhibit hindered internal rotation. These molecules are difficult to analyze, however it is essential that we understand them to facilitate future research of more complex molecules which also exhibit hindered internal rotation.

Another reason for studying these molecules is the upsurge, since 1968, in the detection of interstellar and circumstellar molecules, including an abundance of methanol and its isotopes. Radioastronomers know that molecular clouds contain most of the mass of gas in interstellar space, and that these clouds are involved in the formation of new stars. New powerful millimeter and sub-millimeter wave spectroscopic studies have largely been responsible for this continuing progress. Discovery of new molecules by astronomers requires state of the art laboratory spectroscopic investigation of these molecules. In addition these molecules have been detected in atmospheric measurements above several wildfires in the pacific northwest and they have been used, by astronomers, as temperature probes to study the excitation conditions in interstellar clouds. Correct interpretation of the data is rather crucial and involves a good understanding of the laboratory properties of these molecules. One of the latest reasons for studying these mole-

cules is that after the invention of the optically pumped laser in 1972, it was found that methanol and its isotopes are the richest and most efficient active molecular laser mediums known, producing thousands of distinct laser lines in the FIR region.

The FIR laser used in our laboratory, to obtain high resolution Stark spectra, is a direct discharge molecular gas laser. It consists of an anode and a cathode chamber connected by a 10 ft. long Pyrex glass tube. A 5000 V power supply produces a current ranging from 0.7 to 1.5 Amps, depending on the source gas used, with 2000 V across the laser and 3000 V dropped across a current regulator. Laser operation can be performed with the following source gases; HCN (nitrogen and methane or hydrogen and cyanogen), DCN (deuterium and cyanogen), H<sub>2</sub>O (hydrogen and water), and D<sub>2</sub>O (deuterium and deuterated water). Using these media the laser is capable of producing several fixed frequency lines in the FIR region. These lines are  $\lambda = 337$  and  $311 \mu\text{m}$  for HCN,  $\lambda = 195$ ,  $195'$ , and  $190 \mu\text{m}$  for DCN,  $\lambda = 118 \mu\text{m}$  for H<sub>2</sub>O, and  $\lambda = 107 \mu\text{m}$  for D<sub>2</sub>O.



The FIR beam is coupled out of the laser cavity using a 45° diagonal brass mirror. The beam is then split into a primary and secondary beam. The secondary beam is sent directly into a Golay cell detector, and is used to monitor the output of the laser. The primary beam is sent through two polyethylene lenses which focus it into the Stark spectrometer. Upon exiting the Stark spectrometer the FIR beam is sent through two additional polyethylene lenses which focus the beam into the main Golay cell detector. The signal from this main detector is sent to a lock-in amplifier and then recorded using an x-y plotter. Since the FIR laser produces a fixed frequency beam, a technique known as the Stark effect is necessary to tune the molecular absorption lines into resonance with the laser frequency.

The Stark spectrometer is composed of two parallel plates of silvered glass, 7.5 cm wide, 60 cm long, and separated by  $(0.051508 \pm 0.00005)$  cm using fused quartz spacers. These plates are enclosed in a stainless steel cylinder with .01 mm mylar windows at each end. By applying a uniform electric field (up to 60,000 V/cm) between the Stark plates, molecular absorption lines can be brought into resonance with the fixed laser frequency.

Using this experimental setup, Stark spectra has been observed for methanol and many of its isotopic species including the totally deuterated species CD<sub>3</sub>OD. Several transitions for CD<sub>3</sub>OD were assigned through the analysis of this spectra including the  $J = 11-19$  members of the Q-branch multiplet  $J_k = J_{11} \leftarrow J_{10} E_2 v_t = 0$ . These results

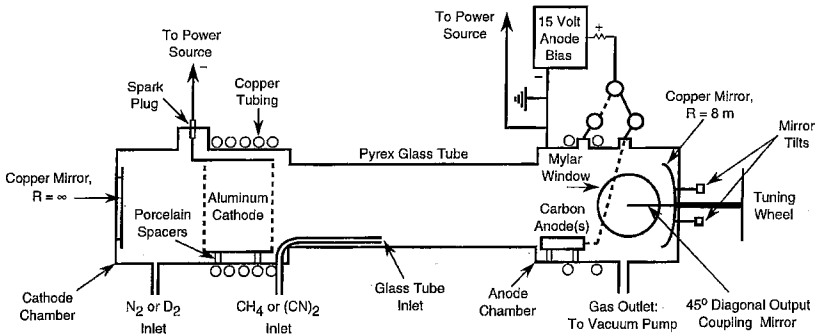
were published in the *Journal of Molecular Spectroscopy* Vol. 147, pages 243-251 (1991). Recently, the Fourier transform far infrared (FTFIR) spectra for the totally deuterated isotopic species  $\text{CD}_3\text{OD}$ , were recorded at the Justus Liebig Universität, in Geissen, Germany. Several transitions previously assigned in the laser Stark spectra, were identified and measured in the FTFIR spectra to an accuracy of  $\pm 6$  MHz. By combining these two sources of data for the  $J = 13$  and  $14$  members of the Q-branch multiplet  $J_k = J_{11} \leftarrow J_{10}$   $E_2$   $v_t = 0$ , the  $\mu_a$  component of the electric dipole moment was calculated for the first time, in the FIR region with high  $J$  and  $K$  quantum numbers.

I would now like to acknowledge the University of Wisconsin-La Crosse (UW-L) for providing partial funding for this project through their undergraduate research grant program. I have also presented this work at the following poster sessions: University of Wisconsin-La Crosse's 1st Annual Undergraduate Research Day, in La Crosse, WI on March 25th, 1998; the Council on Undergraduate Research's (CUR's) 2nd Annual Poster Session on Capitol Hill in Washington, D.C. on April 21st, 1998; and the 66th Annual Meeting of the Minnesota Academy of Science in Winona, MN on May 1st, 1998; also, an oral presentation was given at Argonne National Laboratory in Chicago, IL November 1997.

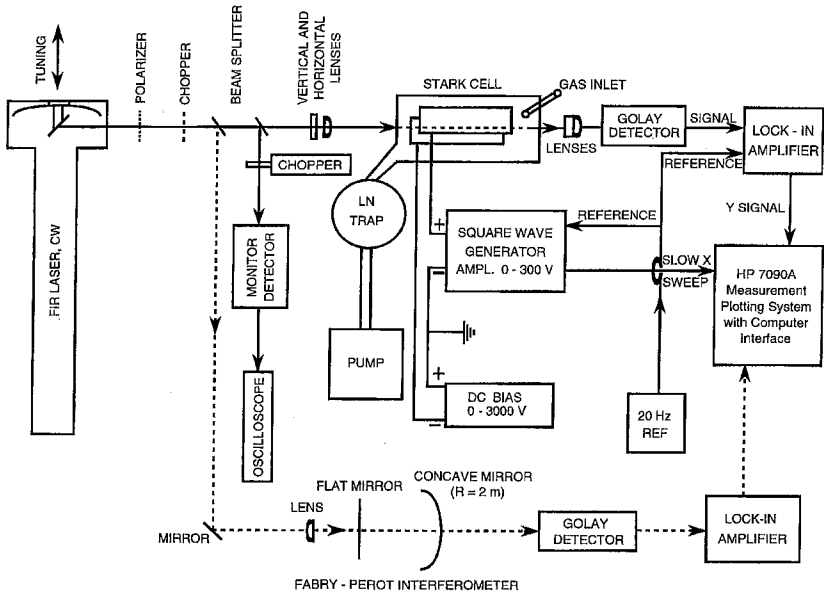
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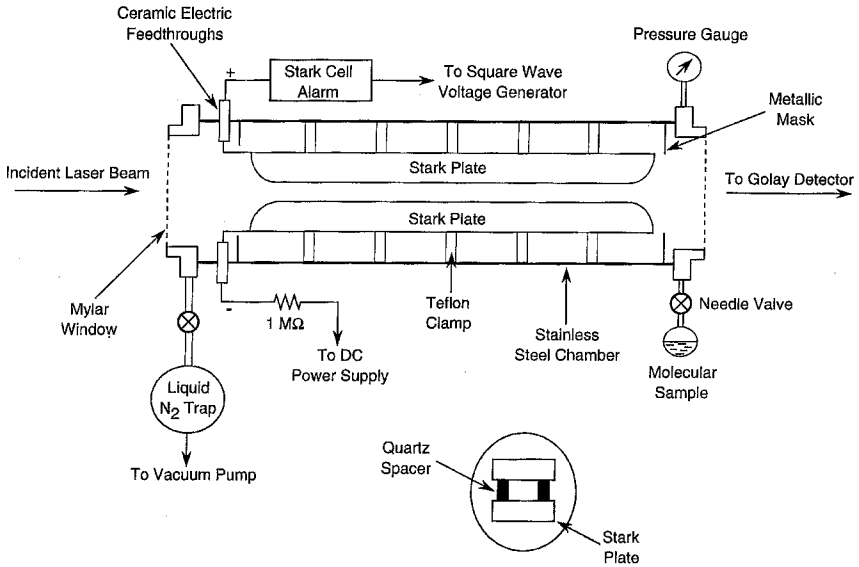
## I. FAR-INFRARED DIRECT DISCHARGE MOLECULAR GAS LASER



## II. EXPERIMENTAL SYSTEM



### III. STARK SPECTROMETER



### IV. DIAGRAM OF CD<sub>3</sub>OD MOLECULE

