

**Title:** Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere

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**Abstract of Research Objectives:**

We obtain quantitative laboratory spectroscopic measurements of molecular constituents which are of importance in understanding the "health" of the Earth's atmosphere, and in particular emphasize those species which are important for understanding stratospheric kinetics or are used for long term monitoring of the stratosphere. Our measurements provide: (1) line and band intensity values which are needed (a) to establish limits of detectability for as yet unobserved species and (b) to quantify the abundance of those species which are observed, (2) line-positions, -half widths and pressure induced shifts are all needed for remote sensing techniques, and (3) data on the above basic molecular parameters at temperatures and pressures appropriate for the real atmosphere.

**Summary of Progress and Results:**

The Herman-Wallis effect was used to obtain absolute line intensities for a number of free radical diatomic molecules: at the end of 1987 journal articles were published on absolute ro-vibrational intensities for the  $\text{C}\ell\text{O}$  and  $\text{CS}$  radical species and subsequently absolute ro-vibrational line intensities have been determined for the  $\text{NH}$  and  $\text{SH}$  molecules. We are currently working on spectra of  $\text{OH}$  which in one scan extend from the pure rotational region, starting about  $350\text{ cm}^{-1}$ , thru the  $\Delta V=1$  ro-vibration bands which are centered around  $3500\text{ cm}^{-1}$ . We hope to obtain absolute line intensities with this data using a generalized Herman-Wallis approach. We have made low temperature  $\text{N}_2$  - broadening measurements on  $\text{O}_3$  lines in the  $1040\text{ cm}^{-1}$  spectral region using a 6 cm teflon coated low temperature cell. The construction of a 30 cm low temperature absorption cell is nearly completed. It is made of copper with an acid resistant stainless steel liner and should be coolable to 150 K. Diode laser spectra have been obtained of highly purified samples of  $\text{C}\ell\text{ONO}_2$  in the  $780.2\text{ cm}^{-1}$  spectral region. Some structure in these spectra offer hope that the intensities can be understood at the line by line level. Laboratory spectra obtained at Kitt Peak (with L. Brown, J.P.L.) on the  $1450\text{ cm}^{-1}$  band of  $\text{CH}_3\text{C}\ell$  will be used to estimate atmospheric abundance from ATMOS spectra.

**Journal Publications(1988-1989):**

1. S.D. Gasster, C.H. Townes, D. Goorvitch and F.P.J. Valero, "Foreign-gas collision broadening of the far-infrared spectrum of water vapor", *J. Opt. Soc. B.* **5**, 593 (1988).
2. C. Chackerian, Jr., "The Determination of Absolute Ro-vibrational Intensities for Radical Diatomic Molecules", *J. Quant. Spectrosc. Rad. Transfer* **40**, 195 (1988).
3. C. Chackerian, Jr., G. Guelachvili, A. Lopez-Piniero and R. Tipping, "Ro-vibrational Intensities for the  $\Delta V = -1$  bands of the  $\text{X }^3\Sigma$   $\text{NH}$  radical: experiment and theory", *J. Chem. Phys.* **90**, 641 (1989).
4. C. Chackerian, Jr., D. Goorvitch and L. Giver, " $\text{N}_2$ -broadening in the  $\text{HCL}$  Vibrational Fundamental: Temperature Dependence between 160 and 296 K", *J. Quant. Spectrosc. Rad. Transfer* (submitted).
5. C. Chackerian, Jr., N. Lacombe, A. Levy, Collisional Line Mixing, in "Spectroscopy of the Earth's Atmosphere and Interstellar Molecules" (K. N. Rao and A. Weber, eds) Academic Press (in press).