

**Theoretical Studies of Spectroscopic Problems of Importance for
Atmospheric Radiation Measurements**

by

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Many of the instruments used to deduce the physical parameters of the Earth's atmosphere necessary for climate studies or for pollution monitoring (for instance, temperature versus pressure or number densities of trace molecules) rely on the existence of accurate spectroscopic data and an understanding of the physical processes responsible for the absorption or emission of radiation. During the summer, research was either continued or begun on three distinct problems: 1) an improved theoretical framework for the calculation of the far-wing absorption of allowed spectral lines; 2) a refinement of the calculation of the collision-induced fundamental spectrum of N_2 ; and 3) an investigation of possible line-mixing effects in the fundamental spectrum of CH_4 . Progress in these three areas is summarized below.

During the past few years, we have developed a theoretical framework for the calculation of the absorption of radiation by the far wings of spectral lines. Such absorption due to water vapor plays a crucial role in the greenhouse effect as well as limiting the retrieval of temperature profiles from satellite data. Several improvements in the theory have been made and the results are being prepared for publication.

Last year we published results for the theoretical calculation of the absorption of radiation due to the dipoles induced during binary collisions of N_2 molecules using independently measured molecular parameters; the results were in reasonable agreement with experimental data. However, recent measurements have revealed new fine structure that has been attributed to line-mixing effects. We do not think that this is correct, rather that the structure results from short-range anisotropic dipoles. We are in the process of including this refinement in our theoretical calculation in order to compare with the new experimental data.

Subtle changes in the spectra of CH_4 measured by researchers at Langley have also been attributed to line-mixing effects. By analyzing the same spectral lines broadened by air and by N_2 , and by studying different spectral lines, we have attempted to verify or rule out possible line-mixing mechanisms. Due to the complexity and richness of the spectrum of this highly symmetric molecule, as well as the small magnitude of the effects, a detailed first-principle calculation of the mixing is a difficult problem. Before such a program is undertaken it is important to glean as much information as possible concerning the possible mechanisms by a systematic analysis of the existing data.