TIME-RESOLVED ROTATIONAL ENERGY TRANSFER AND SPECTRAL LINE BROADENING IN ACETYLENE. A HIGH RESOLUTION RAMAN STUDY.

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The *quasi*-cw stimulated Raman technique is a powerful tool for the determination of collisional broadening and line-mixing parameters, which bear a very direct relationship with the rotational energy transfer rate constants matrix at the state-to-state level. Indeed, the broadening coefficients and the analysis of line-mixing profiles, frequently combined with a rate-law analysis, have provided a wealth of information on collision physics for many gas systems throughout the years. We report on new high resolution measurements of the broadening coefficients on the Q-branch of the ν_2 band of acetylene.

Furthermore, last year at this meeting, we reported on a new technique for the determination of state-to-state rotational energy transfer rate constants. based on a time-resolved double-resonance Raman-Raman scheme. It uses the *quasi*-continuous stimulated Raman-loss technique for the probe stage. Through a systematic recording of the time evoultion of rotational populations from a single initially pupulated J level, it allows the direct determination of most elements of the rate-constant matrix without resorting to fitting or scaling laws.

The comparison of the results obtained from from the high resolution spectroscopic approach with those from the time-resolved dynamics experiment provides insight into the collision mechanisms and some of the assumptions or simplifications usually made in rate-law analysis.