AN ANALYTIC EXPRESSION FOR THE MOLECULAR EMISSION SIGNAL OBSERVED IN COAXIAL-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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Transient microwave spectroscopy was introduced by Dicke and Romer[a,b] approximately 40 years ago. In the early eighties, Balle, Flygare, and coauthors developed a time-domain microwave spectrometer based on a pulsed supersonic gas expansion perpendicular to the axis of a Fabry-Perot resonator[c], and provided theoretical expressions for the shape of the observed transient molecular signal[d,e]. Since the velocity equilibration of the molecules during the gas expansion minimizes Doppler and pressure broadening, the achievable linewidth in such an experiment should be very small. Unfortunately, the short transit time of the polarized gas through the small active region of the cavity limits the resolution. Both sensitivity and resolution of the spectrometer can be greatly improved by a coaxial arrangement of the microwave resonator and the gas expansion source[f]. Due to the propagation of the molecular beam along the symmetry axis of the mirrors, both the transit time through the active region of the cavity and the volume of the gas ensemble interacting with the active region of the resonator are maximized. With this arrangement, the lines of the molecular emission signal appear in the frequency domain as completely resolved doublets with individual linewidths of approximately 1kHz (HWHM). The experimental results are explained using the density matrix formalism to yield expressions analogous to the optical Bloch equations. An analytical function for the shape of the free induction decay (FID) of the molecular signal is derived by calculating the transient electrical field using Maxwell's equations.

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