MOLECULAR STARK EFFECT MEASUREMENTS IN BROADBAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTROMETERS

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We demonstrate the implementation of molecular Stark effect measurements in broadband, chirped-pulse Fourier transform microwave (CP-FTMW) spectrometers. For broadband spectroscopy, the dipole moment determination is performed by measuring the full, broadband spectrum (7 - 18 GHz) at a single electric field strength. The electric field strength is calibrated internally using the first order Stark shift of trifluoropropyne (2.317 D) which is added in a trace amount to the sample mixture. The molecular rotational spectrum in the applied electric field is fit to the rotational Hamiltonian with the rotational and distortion constants fixed at their field-free values. The only parameters varied in the fit are the Stark interaction terms ($\mu \cdot E$) along each principal axis direction. The open interaction region available in CP-FTMW spectrometers makes it easy to incorporate simple electrode designs in the spectrometer. We use the "Stark cage" design previously described by Emilsson *et al.*[a] We illustrate the effects of field inhomogeneity on broadband measurements. The performance of broadband molecular Stark effect measurements is benchmarked by comparing the new results to previous cavity-FTMW dipole moment determinations that track individual rotational transitions at several field strengths. The potential advantages of the broadband technique are suggested by the broadband Stark measurements of OCS where the dipole moments of several isotopomers and complexes are obtained from a single data set.

[a]Emilsson, T. *et al.*, *J. Chem. Phys.* **112** (2000), 1287-1294