STATE-TO-FIELD VIBRATIONAL ENERGY TRANSFER FROM S_1 *PARA*-DIFLUOROBENZENE WITH HIGH VIBRATIONAL EXCITATION. ABSOLUTE COLLISION CROSS SECTIONS AND QUANTAL EFFECTS.

TODD A. STONE and CHARLES S. PARMENTER, *Indiana University Department of Chemistry, Bloomington, Indiana 47405*.

State-to-field vibrational energy transfer (VET) from several high lying levels ($E_{vib} > 2800$ cm^{-1}) within the S_1 ($^1B_{2u}$) manifold of *para*-difluorobenzene (*p*DFB) vapor at 300 K in single collisions with Ar and He is probed. A laser pump-dispersed fluorescence probe approach provides absolute collision cross sections for this large molecule (30 modes) in a region where the vibrational state density approaches 10^4 per cm^{-1}. In this region, *p*DFB is beginning to acquire the characteristics typical of high energy thermal unimolecular reactions, namely an enormous state density and highly mixed vibrational identities. Additionally, we have developed a technique based on electronic state quenching using molecular oxygen (chemical timing)[a] by which we may investigate the behavior of the cross section as the mixed character of the pumped level is deliberately tuned. Tuning the vibrational character of the pumped level for a series of VET interactions provides the unique view of how (or whether) quantal effects influence VET in regions of large state density.

[a] R. A. Coveleskie, D. A. Dolson, and C. S. Parmenter, *J. Phys. Chem.*, **89**, 645 (1985).