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

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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.