

ABSOLUTE CROSS SECTIONS FOR VIBRATIONAL ENERGY TRANSFER IN THE QUASI-CONTINUUM OF
PARA-DIFLUOROBENZENE.

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These experiments yield basic information for kinetic models of the activation/deactivation step of thermal unimolecular reactions. For these highly excited vibrational levels where the high state density approaches a quasi-continuum and where state mixing is significant, a special technique based on oxygen fluorescence quenching (chemical timing)^a is used. Absolute cross sections are measured for vibrational energy transfer (VET) from a wide range of S₁ levels of *para*-difluorobenzene (*p*DFB) as it undergoes single collisions with rare gases. The highest region so far studied has densities of about 10⁴ levels per cm⁻¹. The study involves preparing *p*DFB in a narrow vibrational region and monitoring fluorescence as VET with Ar occurs into a field of surrounding vibrational levels. All of the cross sections so far observed are less than the Lennard-Jones value that is often assumed for modeling the unimolecular problem. Some exceed hard sphere values.

^aR. A. Coveleskie, D. A. Dolson, and C. S. Parmenter, *J. Phys. Chem.*, **89**, 645 (1985).