

USING CHEMICAL TIMING TO OBTAIN VIBRATIONAL ENERGY TRANSFER CROSS-SECTIONS IN THE VIBRATIONAL CONTINUUM REGION OF *para*-DIFLUOROBENZENE

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Our experiments yield the absolute single-collision cross-section values for state-to-field vibrational energy transfer (VET) between *para*-difluorobenzene (*p*DFB) vapor and various inert gases. Currently, we are probing levels with 3700cm^{-1} of vibrational energy where the state density of order 10^4 per cm^{-1} establishes a quasi-continuum. The accompanying intramolecular vibrational redistribution (IVR) blocks the use of conventional VET techniques. We have incorporated the well established chemical timing procedure in our VET measurements. In the midst of overwhelming IVR, it enables us to generate the vibrational structure needed to gain access to cross-section measurements. The resulting chemical timing VET experiments, based on electronic state quenching by molecular oxygen, are capable of providing cross-sections in the regions where the state density is enormous. Thus, this study enables us to gain insight into cross-section sizes involved in thermal activation/deactivation of large molecules undergoing unimolecular reactions, and also to understand how these cross-sections depend on vibrational energy content, state density and collision partner. A revealing comparison with usually assumed Lennard-Jones values will be made.