STATE-TO-STATE INELASTIC SCATTERING FROM S_1 GLYOXAL WITH THE RARE GAS SERIES: UNIFORM ROTATIONAL VS. CHANGING VIBRATIONAL CHANNEL COMPETITION.

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A crossed molecular beam and laser pump-dispersed fluorescence probe approach was used to measure state-to-state relative cross sections from S_1 glyoxal (CHO-CHO) collisions with H_2 and the entire rare gas series. The relative cross sections were obtained from experiments in which a laser prepares S_1 glyoxal in the 0^0 K = 0 state with J = 0 - 10. Dispersed S_1 - S_0 fluorescence was used to monitor inelastic scattering to more than 25 rotational and rovibrational destination states with K resolution. Inelastic cross sections were then extracted by computer simulation of the fluorescence spectra. The results indicate that rovibrational inelastic scattering is highly selective in that it involves only $\nu_7 = +1$ where $\nu_7 = 233$ cm^{-1} is the lowest frequency mode. Despite large variations in the collisional kinematics and in the interaction potential energy surfaces, the competition among rotationally inelastic channels is essentially identical for the gases Ne, Ar, Kr and Xe. In turn, those cases differ from H_2 and He solely by the fact that orbital angular momentum constraints with the light gases limit scattering to only those states with K = 15. In contrast, the competition between rotational and rovibrational scattering changes with the collision partner to the extent that state-to-state resolution of rovibrational scattering is not possible for Ar, Kr and Xe. Previous theoretical predictions for Ar inelastic scattering are consistent with earlier arguments that this competition is dominated by kinematic factors rather than by variations in the interaction potential.