

OBSERVATION OF NEW DYNAMICS IN THE STATE-RESOLVED COLLISIONAL RELAXATION OF HIGHLY EXCITED MOLECULES

GERALDINE O. ECHEBIRI, MATTHEW SMARTE, WENDELL W. WALTERS, JILL M. CLEVELAND, CHRISTINE MCCARL, ALICE KUNIN and AMY S. MULLIN, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.*

The dynamics of collisional deactivation of highly energized molecules, pyrazine-h₄ and pyrazine-d₄, by HCl molecules at 300 K show evidence of a new mechanism for collisional energy transfer. Highly vibrationally excited ($E_{vib} = 37,900 \text{ cm}^{-1}$) pyrazine-h₄ and pyrazine-d₄ molecules are produced in separate experiments by pulsed excitation with the fourth harmonic output of a Nd:YAG laser at $\lambda = 266 \text{ nm}$. Collisions between the energized isotopes and HCl molecules are monitored by measuring the nascent transient IR absorption of scattered HCl in individual rotational states. The results indicate that HCl molecules are scattered with a gain in rotational and translational energy, but the largest recoil energies are observed for the lowest rotational energy states of HCl. This behavior is opposite to that seen for other bath molecules including DCl and CO₂. The results point to differences in intermolecular interactions between the energy donor and acceptor molecules as contributing factors to the observed differences in the mechanism of energy transfer.