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Vibrationally Enhanced Reactions of Highly Excited Pyridine-d$_5$ (E$_{vib}$=38,000 cm^{-1}) with Cl Radicals AMY MULLIN, ZIMAN LI, QINGNAN LIU, University of Maryland — High resolution transient IR probing of DCl reaction products at 4.9 μm is used to study the influence of large amounts of internal energy on D-atom abstraction reactions of pyridine-d$_5$ (E$_{vib}$=38,100 cm^{-1}) with Cl radicals. Vibrationally hot pyridine-d$_5$ molecules are prepared using 266 nm pulsed excitation and Cl radicals are generated by photodissociation of Cl$_2$ at 355 nm. Cl radicals undergo collisions with pyridine-d$_5$ with E$_{rel}$=2990 cm^{-1} which is near ΔH$_{rxn}$=3050 cm^{-1}. The D-atom abstraction rates are enhanced by a factor of 200-300 when the pyridine reactant is vibrationally excited. Energy measurements of the products show that the pyridinyl radical has lost only one quantum of the C-D stretch. We find that the reaction mechanism is direct with a linear transition state. The lack of energy equilibration among the reaction products highlights the local nature of the transition state and shows that most of the pyridine vibrational energy is not available to the reaction. The experimental results are compared to phase space theory calculations that predict a vibrational enhancement of $\sim$10^6-10^8.

Amy Mullin
University of Maryland

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