PHOTOGENERATION OF, AND EFFICIENT COLLISIONAL ENERGY TRANSFER FROM, VIBRATIONALLY EXCITED HYDROGEN ISOCYANIDE (HNC)

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Time-resolved IR emission spectroscopy has previously been used to characterize the 193 nm photodissociation dynamics of vinyl cyanide, $H_2CC(H)CN$[b]. Of significance, it was observed that the major molecular elimination channels generated ro-vibrationally excited photofragments consisting of: HCN + $H_2CC$: and HNC + HCCH, for which the HCN / HNC branching ratio was deduced to be 3.3 to 1. In the present study, we examine the collisional deactivation of the vibrationally excited ($E_{vib}$=15 kcal mole$^{-1}$ above the zero-point energy) $\nu_1$ NH and $\nu_3$ NC stretches of HNC, in response to collisions with a series of inert rare-gas atoms: Rg=He, Ar, Kr, and Xe. Spectral modeling of the IR emission allows direct determination of the time-dependent average internal energy of HNC, and therefore a quantification of the average energy lost per collision, as a function of the internal energy. Similar to vibrationally excited radicals[c], collisional deactivation of HNC is shown to be remarkably efficient, likely due to comparatively strong HNC / Rg intermolecular attractive interactions. Subsequently, depending upon the relative rates, excited HNC can either isomerize to the energetically more stable HCN, or be rapidly quenched and kinetically trapped as HNC. Potential implications for the astrophysical HNC / HCN abundance ratio problem will be discussed.

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