DIRECT STATE-SELECTIVE MEASUREMENT OF THE COOLING RATES OF VIBRATIONALLY EXCITED $1^3\Sigma^+_g$ $N\alpha_2$ ON THE SURFACE OF HELIUM CLUSTERS

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Optical excitation of the $(\nu' = 10)\ 1^3\Sigma^+_g \leftarrow 1^3\Sigma^+_u$ transition of $N\alpha_2$ formed on a He cluster surface yields dispersed emission which can only be modeled by including significant contributions from all $(\nu' = 0 - 10)$ lower vibrational levels of the excited electronic state. The process by which this vibrational energy is transferred from the excited dimer to the He nanodroplet has been characterized using state-selective time-correlated single photon counting. We have measured the onset of fluorescence arising from lower $\nu'$ levels upon excitation of various higher vibrational states and find that in all cases fluorescence begins in less than 250 ps. Along with the non-exponential nature of the distribution of level populations, this leads us to conclude that the vibrational energy is not transferred in a cascading process but rather by means of multiquanta jumps. Following the vibrational deexcitation, the dimer emits in the gas phase, having desorbed from the cluster surface.