We report on the observation of blue-detuned photoassociation as proposed in [1] and references therein. “Blue-detuned” refers to the location of vibrational levels — energetically above the corresponding atomic asymptote. Ultracold $^{85}\text{Rb}$ atoms in a MOT were photoassociated to levels of the $1^{3}\Pi_g$ state a few hundred wavenumbers above the $5S + 5P_{3/2}$ limit. These transitions were found to be strong even though they occur at short internuclear separations ($R_{e}=10a_0$). Levels of the $1^{3}\Pi_g$ state spontaneously decay to the $a^{3}\Sigma_u^+$ state, where they are detected by resonantly enhanced multiphoton ionization with time-of-flight spectroscopy. We have observed most vibrational levels of the $1^{3}\Pi_g$ state belonging to all of its spin-orbit components ($0^+_g, 0^-_g, 1_g, 2_g$). Recent unpublished ab-initio calculations [2] of these potentials show good agreement with the observed vibrational and rotational constants. This work is supported by the NSF, AFOSR, and UConn Research Foundation.

[2] O. Dulieu, private communication