Resolved laser induced fluorescence spectra of NiD, recorded at Doppler resolution between 11500 and 18000 cm$^{-1}$, have defined some 200 term energies in two of the three strongly-interacting, low-lying ($X^{2}\Delta$, $W^{2}\Pi$ and $V^{2}\Sigma^{+}$) states of NiD associated with an Ni$^+$(3d$^9$)-D$^-$ configuration. Our observations span $v = 0-5$ in the lowest spin-orbit component of the ground state, $X_1^{2}\Delta_{5/2}$, $v = 0-3$ in $X_2^{2}\Delta_{3/2}$ and $v = 0-1$ in $W_1^{2}\Pi_{3/2}$, the lower component of the $W^{2}\Pi$ state. Spin-orbit and rotation-electronic interactions are strong in NiD. Large parity splittings are seen, due to interactions with the unobserved $^{2}\Sigma^{+}$ state. We have attempted a global, multi-isotope fit to reproduce observed term energies up to 6000 cm$^{-1}$ in NiD and $^{58,60,62}$NiH, in an extension of the ‘Supermultiplet’ model proposed by Gray and co-workers $^{a}$, because fits with NiD term energies alone failed to converge to sensible solutions. Dunham-type parameters have been used to represent the unperturbed $X^{2}\Delta$, $W^{2}\Pi$ and $V^{2}\Sigma^{+}$ states, with off-diagonal matrix elements (treating spin-orbit, $L$- and $S$-uncoupling effects) based on Ni$^+$ atomic properties. Some electronic Born-Oppenheimer breakdown terms were included in the model.

The spectra show emission from several excited states close to the unique level populated by the single-mode laser. Bands of collisionally-induced fluorescence identify three levels ($A$ ($\Omega = 5/2$) $v = 1$, $E$ ($\Omega = 3/2$) $v = 1$ and $I$ ($\Omega = 3/2$) $v = 0$) that have not been reported before.

$^{a}$Gray, Li, Nelis, and Field, J. Chem. Phys. 95, 7164 (1991)