A new mechanism is described for recording optical spectra of molecules in helium nanodroplets. This “hot molecule” technique is applicable when optical excitation leads to a long-lived metastable excited state inside a helium droplet, which in turn changes the electron impact ionization cross section of specific ion product channels. This is illustrated by electronic excitation of toluene to its S1 state, which undergoes intersystem crossing into a long-lived triplet state with high quantum yield. By monitoring different ions, spectra in both depletion and enhancement modes have been obtained. The technique has potential for applications whenever optical excitation delivers a relatively long-lived (ms or longer) excited state and therefore complements existing depletion techniques, which require fast dissipation of energy into the helium matrix.