PHOTOELECTRON SPECTROSCOPY OF ClH_2^- AND ClD_2^-: A PROBE OF THE Cl + H_2 VAN DER WAALS WELL AND SPIN-ORBIT EXCITED STATES

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The anion photoelectron spectra of ClH_2^- and ClD_2^- were measured at 299 nm, accessing the prereactive van der Waals well on the ground state Cl + H_2 potential energy surface, as well as the low-lying spin-orbit excited states resulting from the interaction of Cl ($^2P_{3/2}$) and Cl^* ($^2P_{1/2}$) with H_2. The photoelectron spectra are dominated by two relatively narrow peaks corresponding to the transitions to the neutral $Cl{\cdot}H_2$ and $Cl^*{\cdot}H_2$ complexes both are shifted toward higher electron binding energy relative to atomic chlorine due to the solvent shift by the hydrogen. Another feature in the spectra is the relative broadening of ClD_2^- versus ClH_2^-. The broadening of the ClD_2^- peaks may have its origins in the excited state transitions. The broadening may also be in part due to the presence of two nuclear spin species, as opposed to one in ClH_2^-. Only ClH_2^- (ortho) was generated in this experiment, while ClD_2^- had both ortho and para complexes generated.