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The hydroxyl radical, OH, is a prototypical open-shell diatomic molecule that is important in a variety of fields, including atmospheric chemistry, interstellar chemistry, crossed beam molecular collision studies, and Stark deceleration. In laboratory studies, OH is commonly detected with rotational state selectivity by measuring laser-induced fluorescence from ultraviolet $A^2\Sigma^+ - X^2\Pi$ transitions. Previous studies have determined the absolute frequencies of these transitions to within approximately $0.003~{\rm cm}^{-1}(100~{\rm MHz})^a$. This level of accuracy is quite sufficient for excitation with commonly-used frequency-doubled pulsed dye lasers, which typically have a bandwidth on the order of $0.1~{\rm cm}^{-1}$, but for driving the transitions with a continuous-wave (CW) laser with a linewidth on the order of 1 MHz or less, the transition frequencies must be known much more exactly.

In this talk, I would like to present our recent high-precision measurements of the $A^2\Sigma^+, v'=0 \leftarrow X^2\Pi_{3/2}, v''=0, J''=3/2$ transitions in $^{16}\mathrm{OH}$ and $^{16}\mathrm{OD}$. Using a frequency-doubled CW dye laser which is stabilized and monitored with the help of an optical frequency comb, we have measured transitions to the 12 lowest levels of the $A^2\Sigma^+, v'=0$ vibronic state of $^{16}\mathrm{OH}$ with an uncertainty of less than $100~\mathrm{kHz}$ (10^{-10} relative uncertainty) and are currently completing measurements of transitions to the 16 lowest A levels in $^{16}\mathrm{OD}$ with an expected uncertainty of 100– $200~\mathrm{kHz}$. These measurements have enabled us to determine the $^{16}\mathrm{OH}$ $A^2\Sigma^+, v'=0$ band origin with three orders of magnitude higher precision and the rotational constant with two orders of magnitude higher precision than previously possible. Similar improvements are expected in the corresponding constants of $^{16}\mathrm{OD}$, as well as in its spin-rotation constant γ , which has not been measured in microwave double-resonance experiments as in $^{16}\mathrm{OH}$ b .

^aG. Stark et al. J. Opt. Soc. Am. B, 11:3-32, 1994

^bJ. J. ter Meulen et al. Chem. Phys. Lett., 129:533–537, 1986