# THEORY OF NEAR-RESONANT INTRACAVITY ENHANCED TWO-PHOTON ABSORPTION

KEVIN LEHMANN, *Departments of Chemistry and Physics, University of Virginia, Charlottesville, VA, USA*.

All polyatomic molecules have IR allowed fundamentals, $0 \rightarrow \nu_s$, each of which has a corresponding "hot band" $\nu_s \rightarrow 2\nu_s$ that has an origin shifted by $2X_{ss}$ from the corresponding fundamental, where $X_{ss}$ is the diagonal anharmonic spectroscopic constant for mode $s$. There will always be Doppler-free two-photon absorption transitions where a $P(J)$ transition of the fundamental will be nearly resonant with a $R(J-1)$ transition of the hot band. For bands with $Q$ branches, there is also the possibility for near-resonant $Q$ followed by $R$ transitions and for $P$ followed by $Q$ branch transitions. For a linear molecule without missing levels, the maximum detuning from exact 2-photon resonance will be less than $B$, the rotational constant of the molecule. For symmetric and asymmetric tops, the multiple branches increase the probability of a very near resonance. I have derived general expressions for the two-photon absorption cross section for such transitions and have assembled predictions for cases where the necessary data is available in HITRAN.

The resonant enhancement combined with the intracavity intensity enhancement leads to cases of strong and selective two-photon absorption, particularly at low pressure, in some cases even stronger than one-photon absorption as the entire population of the lower state can be pumped rather than only molecules with Doppler shifts within a power-broadened homogeneous width. The one and two-photon absorption contributions to the cavity decay can be separately fit, uncoupling the two-photon absorption from other sources of cavity lass. I previously published, *App. Phys B* **116**, 147 (2014), an analysis of the expected sensitivity limit of such a combined fit in both the detector noise and shot noise limited cases. Combined with the approximately two orders of magnitude increase in resolution, and the fact that the two-photon absorption spectrum will be extremely sparse due to the near-resonance requirement, this should provide extremely high sensitivity and unprecedented selectivity for trace detection in low-pressure gases.

An experimental apparatus is currently being assembled to experimentally verify these predictions and it is hoped that preliminary data will be available at the time of the meeting.