Pump/Probe measurement of V-V transfer in $\text{O}_2$ and $\text{H}_2$ TAI AHN, Univ of California - Riverside, IGOR ADAMOVICH, WALTER LEMPERT, Ohio State University — We present new sets of V-V rate coefficients for vibrational levels 0 – 5 in $\text{O}_2$ and $\text{H}_2$ at 300 K, using a stimulated Raman – spontaneous Raman pump/probe apparatus. For $\text{O}_2$ it is found that previously reported semi-classical trajectory calculations of Coleti and Billing underestimate the V-V rate coefficients by approximately one order of magnitude, in agreement with recent measurements by of Kalogerakis and the earlier observations of Diskin. For $\text{H}_2$ non-resonant processes, comparison with recalculated semi-classical predictions using the identical potential to that given by Cacciatori and Billing results in predicted rates which are too fast, by a factor of $\sim 2.5$, consistent with the previously reported value of Kreutz. However for the “resonant” V-V process, $\text{H}_2$ (v=1) + $\text{H}_2$ (v=1) $\rightarrow$ $\text{H}_2$ (v=2) + $\text{H}_2$ (v=0), predictions are found to be too slow, by a factor of approximately two, consistent with previous reported data of Farrow and Chandler. This suggests that semi-classical calculation methods that treat the rotational motion classically may be unsuitable for $\text{H}_2$, due to rotational energy level spacings which are comparable to $k_B T$. 

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