SPECTROSCOPY AND DEPERTURBATION OF A THREE-LEVEL FERMI RESONANCE OF THE OH STRETCH OVERTONE IN NITRIC ACID

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The near-IR spectrum of $\mathrm{HONO_2}$ has been recorded in the vicinity of the first OH stretch overtone ($2\nu_1$) under jet-cooled conditions, using a vibrationally mediated photodissociation scheme with detection of chemiluminescence from $\mathrm{NO_2^*}$ fragments. Three vibrational bands were observed with origins at 6933.7, 6938.9 and 6951.7 $\mathrm{cm^{-1}}$ and assigned to strongly interacting states described to zeroth order as $2\nu_1$, $\nu_1 + 2\nu_2$ and $3\nu_2 + \nu_3 + \nu_7$. A deperturbation algorithm was used to extract the Hamiltonian describing the energies and coupling strengths of the three states. Spectral assignments were aided by comparison with predictions of transition frequencies and couplings from second order vibrational perturbation theory performed by Stanton and coworkers. Additional, weaker couplings to a dense background of vibrational levels associated with intramolecular vibrational redistribution (IVR) results in homogenous line broadening, which is compared with a previous time-domain measurement of the IVR rate under thermal conditions by Crim and coworkers.[a]

[a] D. Bingemann, M. Gorman, A. King, and F. Crim, *J. Chem. Phys.* **107**, 661 (1997)