SUB-DOPPLER SPECTROSCOPY OF MIXED STATE LEVELS IN CH_2

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Saturation dip spectroscopy has been used to measure rovibronic transitions in the $\tilde{b}\,^1B_1 \leftarrow \tilde{a}\,^1A_1$ band system of CH_2 at sub-Doppler resolution. The radical was made by 308 nm excimer laser photolysis of a slowly flowing, low-pressure, sample of ketene (CH_2CO), optionally with added inert buffer gas. Typical observed linewidths in the pure precursor are approximately 8 MHz (FWHM), due to a combination of collisional lifetime and pump-probe beam crossing angle. Due to the non-zero ^{1}H proton nuclear spin, CH_2 exists as two distinct variants, ortho-CH_2 with $I_H = 1$ and para-CH_2 with $I_H = 0$. In ortho-CH_2, each rotational level consists of a triplet of hyperfine components corresponding to levels with $F = J, J \pm 1$. Most singlet CH_2 transitions show unresolved hyperfine structure in our experiment, since the largest splitting is due to $\mathbf{I}.\mathbf{J}$ coupling, typically of the order of kHz. However, a small number of rotational levels in the $v = 0$ level of the lower $\tilde{a}$ state are known to be perturbed by accidentally near degenerate[a] $\tilde{X}\,^3B_1$-state levels via spin-orbit coupling. Spectra involving such levels in ortho-CH_2 exhibit resolvable triplet, $\mathbf{I}.\mathbf{S}$, hyperfine splittings, with the splittings providing a direct measure of triplet state character of the level. We have measured hyperfine splittings for a number of pairs of perturbed levels confirming and refining previous estimates of the singlet-triplet mixing coefficients. Measurements of the pressure-dependent saturation recovery rates with different collision partners can give new insights into dephasing, velocity-changing and inelastic collisions relevant to pressure broadening and intersystem crossing mechanisms.
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[a] U. Bley and F. Temps, J. Chem. Phys. **98**, 1058-1072 (1993)