TRANSIENT FREQUENCY MODULATION SPECTROSCOPY OF HCBr

LEAH M. RUSLEN, and ROBERT W. FIELD , *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*; SIMON W. NORTH, and TREVOR J. SEARS , *Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973-5000*.

Halocarbenes are important reactive intermediates in numerous chemical processes, including organometallic and atmospheric reactions. However, halocarbenes are difficult to observe experimentally because of their transitory nature and weak transitions. In addition, their spectra are complicated by vibronic coupling between the two low-lying singlet states, singlet-triplet perturbations due to the small energy separation between the lowest lying singlet and triplet states, and the large amplitude motion of the bending vibration.

Our work has centered on studying these molecules using transient frequency modulation absorption spectroscopy. We recently utilized this technique to obtain rotationally resolved spectra of the HCBr $A\ ^1\mathrm{A}''$ (0,1,0) - $X\ ^1\mathrm{A}'$ (0,0,0) rovibronic transition between 11930 cm^{-1} to 12030 cm^{-1}. Bromomethylene radicals were obtained by 193nm laser photolysis of bromoform in a slow flow system. Utilizing the information gained from this experiment and previous work,[a] we will discuss the structure of the low lying singlet states of HCBr, including the effect of the large amplitude bending vibration and perturbations from possibly nearby triplet levels.

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[a] Bor-Chen. Chang and Trevor J. Sears *J. Chem. Phys.* **105**, 2135 (1996).