THE ROTATIONALLY RESOLVED INFRARED SPECTRUM OF THE ν_1 AND ν_{13} CH_2 STRETCH OF THE ALLYL RADICAL

J. D. DESAIN, S. D. SHARMA, R. I. THOMPSON, R. F. CURL, *Chemistry Department and Rice Quantum Institute, Rice University, Houston, Tx 77054, USA*.

The ν_1, b-type transition, and ν_{13}, a-type transition, of the allyl radical (C_3H_5) have been observed using infrared laser kinetic spectroscopy. The allyl radical was generated by the flash photolysis at 193 nm of the 1,5 hexadiene, and its transient infrared absorption was probed by a cw color center laser. After we began this work, we learned that David Nesbitt's group had observed and analyzed both these bands in an electric discharge pulsed slit jet apparatus. Professor Nesbitt kindly provided us with these low temperature frequencies and spectroscopic constants. However, we found it very difficult to extend his assignments of ν_1 to higher $K_a{}'$ or much higher N. The Q branches for $K_a{}'$ = (5-10) are readily reconizable in our spectra and could be assigned with the aid of ground state combination differences obtained from the ground state constants of the ν_{11} band[a]. However, a $K_a{}'$ dependent offset from the ν_{11} ground state combination differences was found at $K_a{}'$ greater than 5, and a set of somewhat improved ground state rotational constants were obtained by combining the ν_1 data with the ν_{11} data. These high $K_a{}'$ = (4-8) transitions and Nesbitt's $K_a{}'$ = (0-2) transitions were then used to determine the excited state rotational constants for ν_1. Using this data, we could extend the Nesbitt group assignments of ν_1 for $K_a{}'$ = (0,1,2). The $K_a{}'$ = 3 and some $K_a{}'$ = 2 transitions are not yet assigned, possibly due to heavy perturbations in these states caused by mixing of the energy levels of the two bands. Assignment of the $K_a{}'$ = 9 and $K_a{}'$ = 10 transitions has been carried out, although perturbations in these levels prevents inclusion of these lines in the fit. We have not yet attempted to extend the a-type transition assignments due to heavy congestion of transitions near this band's origin and the heavy overlap of the two transitions in general.

[a] E. Hirota, C. Yamada, and M. Okunishi, J. Chem Phys. 97(5), 2963 (1992).