RYDBERG STATES OF ALLYL RADICAL OBSERVED BY ONE- AND TWO-PHOTON RESONANT IONIZATION SPECTROSCOPY

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The vibronic spectrum of allyl radical (CH_2CHCH_2) at 4.9-8.2 eV has been observed using 1+1 and 2+1 resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The allyl radicals were produced in the nozzle of a supersonic jet expansion by the pyrolysis of allyl iodide. The vibronic assignment for the congested $\tilde{B}\ 1^2A_1(\pi \rightarrow 3s)$, $\tilde{C}\ 2^2B_1(\pi \rightarrow 3p_X)$ and $\tilde{D}\ 1^2B_2(\pi \rightarrow n^*)$ bands at 4.9-5.2 eV will be reexamined with aid of the calculated Franck-Condon factors, especially for the weaker transitions at >5.2 eV which were not identified in previous study.[a] Three new electronic bands are observed for the first time and assigned to the $3^2B_1(\pi \rightarrow 3d_{XZ})$, $2^2A_2(\pi \rightarrow 3d_{XY})$ and $3^2A_1(\pi \rightarrow 3p_Z)$ Rydberg states based on the *ab initio* CI calculation.[b] The observed band origins (in eV) at 6.460 (3^2B_1), 6.607 (2^2A_2) and 7.605 (3^2A_1) are compared with the calculated vertical energies of 6.41, 6.62 and 7.55, respectively. Vibrational progressions with the gross spacings of $\sim$420 cm^{-1} are observed in the Rydberg states. The totally symmetric $\angle$CCC bending in the excited state is responsible for the observed progression as that reported in the $\tilde{B}$ state.[c]

[a] D. W. Minsek and P. Chen, J. Phys. Chem., **97**, 13375 (1993).
[b] T. -K. Ha, H. Baumann and J. F. M. Oth, J. Chem. Phys., **85**, 1438 (1986).
[c] A. D. Sappey and J. C. Weisshaar, J. Phys. Chem., **91**, 3731 (1987).