OBSERVATION OF PURELY ROTATIONAL AUTOIONIZATION IN THE IONIZATION THRESHOLD REGION OF METHYL RADICAL

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We have recently discovered an apparent nominal shift in the observed ionization onset of methyl radical, CH_3. The shift shows temperature dependence but cannot be easily rationalized in terms of conventional hot bands. Subsequent modeling of medium resolution spectra suggested that the observed phenomenon most likely originates from unresolved autoionization, where ΔN=-1,-2,... but Δv=0. We have now further explored the region of interest in high resolution, using a VUV laser setup. CH_3 was prepared using a novel laser photodissociation source that produces radicals well-equilibrated at a known temperature. This is an important feature, since it provides a mechanism to control the initial distribution of rotational states and hence the population of higher N states for which this effect is more easily detectible. The new spectra reveal a dense manifold of autoionizing lines and show clear evidence of rarely observed pure rotational autoionization. The observed lines are interpretable in terms of autoionization of rotational levels belonging to high Rydberg states and approaching the adiabatic ionization limit. The interpretation provides insights on the mechanism involved in rotational autoionization. The observed Rydberg series appear to be a continuation of low Rydberg states observed previously in the range 130-220 nm. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.