HIGH-LYING RYDBERG STATES AND IONIZATION POTENTIAL OF VINYL CHLORIDE STUDIED BY TWO-PHOTON RESONANT IONIZATION SPECTROSCOPY

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High-lying Rydberg states of jet-cooled vinyl chloride (C_2H_3Cl) at 7.5-10 eV have been observed using 2+1 resonance-enhanced multi-photon ionization (REMPI) spectroscopy. The vibronic transitions in the ranges of 62500-65000 cm^{-1}, 67000-70000 cm^{-1} and 70000-72500 cm^{-1} are attributed to $\pi \rightarrow$3p, $\pi \rightarrow$3d/$n_{Cl}\rightarrow$3s and $\pi \rightarrow$4p excitations according to the previous assignment by Williams and Cool.[a] Comprehensive analysis for the vibronic transitions is facilitated with the calculation of Franck-Condon factors based on our recently developed theoretical method.[b] Four Rydberg series at 9.5-10 eV are newly observed and tentatively assigned as due to the promotion of a π-electron to the ns (n = 8-13, 20), np (n = 7-11, 18), np′ (n = 6, 7, 10-18, 21) and nf (n = 6-16) Rydberg orbitals. All the four Rydberg series converge to the same limit, *i.e.* the ground state of vinyl chloride cation. The term values of the nf Rydberg series, fitted to Rydberg formula, provide a very accurate adiabatic ionization energy, 80718 $\pm$ 2 cm^{-1}, for vinyl chloride with a quantum defect of δ = 0.02.

[a] B. A. Williams and T. A. Cool, J. Phys. Chem., **97**, 1270 (1993).
[b] A. M. Mebel, Y. -T. Chen and S. H. Lin, J. Chem. Phys., **105**, 9007 (1996).