A UV+VUV MULTIPHOTON IONIZATION SCHEME FOR OH RADICALS[a]

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OH radicals are of significant atmospheric interest as a dominant oxidizing agent in day-time tropospheric chemistry. In this study, a 1+1′ multiphoton ionization (MPI) scheme is employed to record rotationally-resolved spectra of OH radicals via the $A^2\Sigma^+$ resonant intermediate state.[a] UV excitation is used to prepare OH $A^2\Sigma^+$(v=1, *J*, F_i), which is subsequently ionized by a second photon of fixed frequency VUV (118.3 nm), generated by tripling the 355 nm output of a Nd:YAG laser. The mass-selected OH^+ ion signal from 1+1′ MPI is detected using time-of flight mass spectrometry and compared with the laser-induced fluorescence (LIF) signal arising from OH $A^2\Sigma^+$-$X^2\Pi$(1,0) excitation. The MPI signal is observed over a range of UV+VUV total energies, corresponding to various OH $A^2\Sigma^+$ (v=1, *J*, F_i) intermediate states, with relative intensities that differ considerably from LIF. The ion signal is enhanced relative to LIF at combined UV + VUV photon energies consistent with an autoionizing 3*d* Rydberg state that converges on the OH^+ $A^3\Pi$ ion core;[b] direct ionization into OH^+ $X^3\Sigma^-$ is forbidden in a one-photon electric-dipole transition from OH $A^2\Sigma^+$. The MPI intensities have been quantified relative to LIF over the OH $A^2\Sigma^+$-$X^2\Pi$(1,0) region such that this scheme is now applicable for quantitative state-selective detection of OH $X^2\Pi$.

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