A UV+VUV MULTIPHOTON IONIZATION SCHEME FOR OH RADICALS

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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. 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 3d Rydberg state that converges on the OH$^+$ $A^3\Pi$ ion core; 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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