Vacuum ultraviolet (VUV) radiation at 124.8 nm (9.93 eV) was produced from two-photon resonant second harmonic generation (SHG) in a Xeon gaseous medium and used to probe molecular samples of acetone, furan, thiophene, ammonia, and methane. The mass spectra recorded from the species with ionization energies below 9.93 eV were dominated by the parent ions. The parent ions were only observed when the incident UV radiation was tuned to resonate with the two-photon transition $5p^5(^2P_{3/2})6p(^1P_0)$ - $5p^6(^1S_0)$ of Xe at 80119.474 cm$^{-1}$. The pressure dependence and the resonant nature of the parent ions observed support the mechanism for SHG as the ionization-initiated electric field induced SHG via the third-order nonlinear susceptibility, $\chi^{(3)}$, which is enhanced by the coupling between the $5p^5(^2P_{3/2})6p(^1P_0)$ and the nearby $5p^5(^2P_{3/2})6d(^1D_2)$ states of Xe atoms.