

Supporting Information

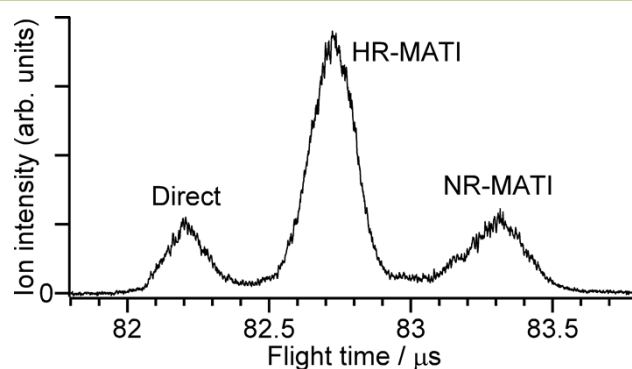


Fig. S1 Splitting of the PhOH–Ar mass peak in the time-of-flight mass spectrometer under application of the negative pulse for the high resolution MATI spectroscopy, setting the total energy ($v_{\text{exc}} + v_{\text{ion}}$) to $IE_0(\pi)$ (68447 cm^{-1}). Each peak provides direct ionization, high resolution (HR)-MATI, and normal resolution (NR)-MATI signal, respectively.

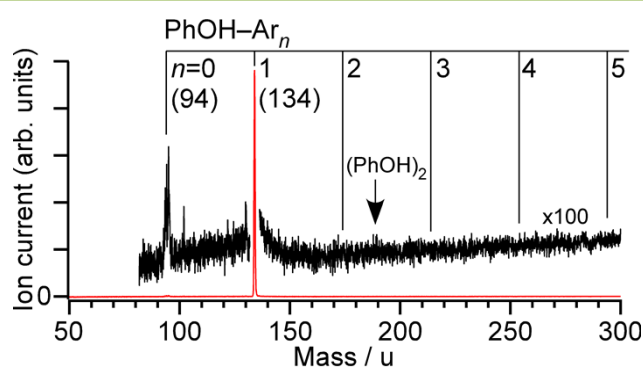


Fig. S2 Time-of-flight mass spectrum of PhOH-Ar_n recorded under the same condition as the MATI-IR spectra described in the text for resonant soft ionization of PhOH–Ar via its S_1 origin.

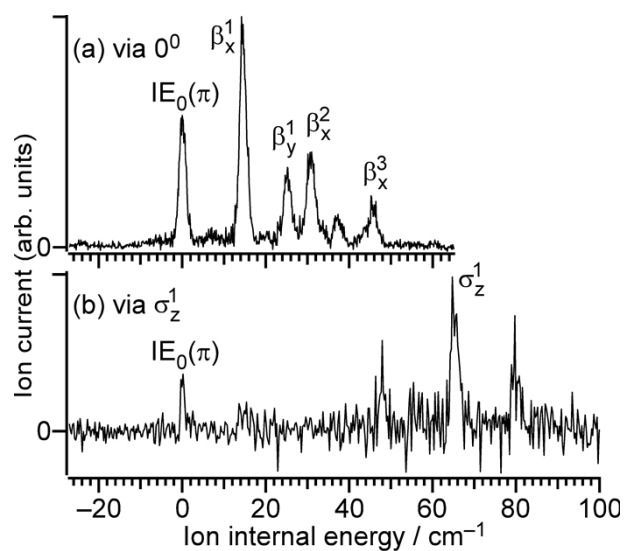
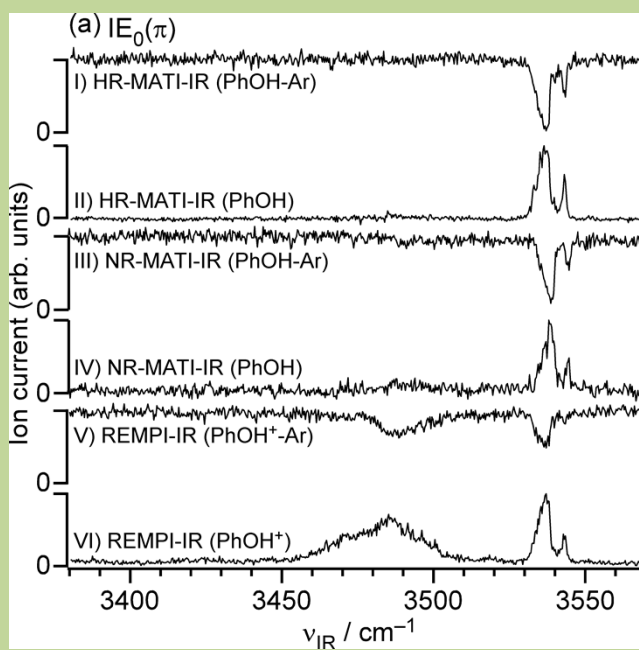
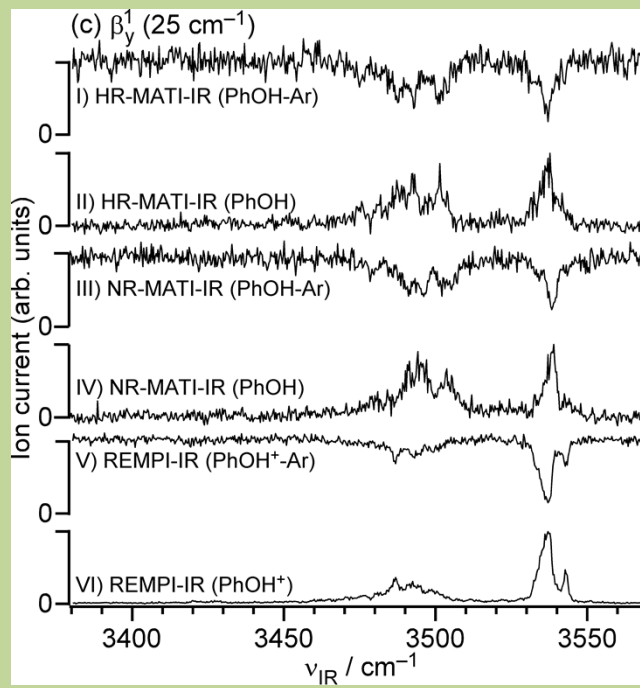
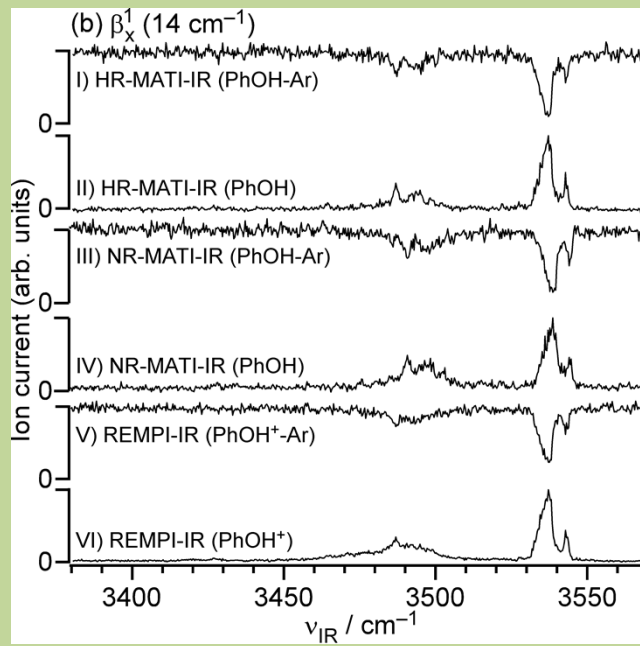


Fig. S3 Comparison between MATI spectra of PhOH–Ar recorded via the (a) 0⁰ and (b) σ_z¹ levels in the S₁ state.





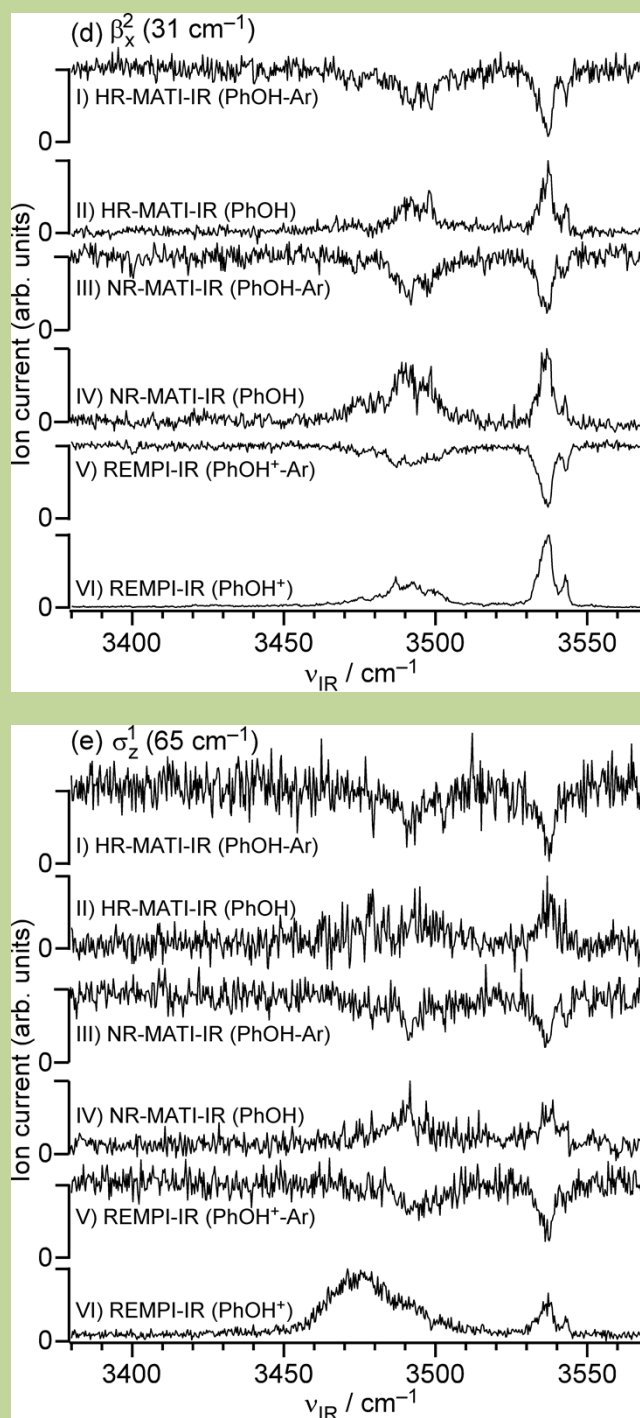


Fig. S4 Comparison between high-resolution MATI monitored IR (HR-MATI-IR (I) and II)), normal-resolution MATI monitored IR (NR-MATI-IR (III) and IV)), and REMPI-IR (V) and VI)) spectra of PhOH–Ar monitored in the PhOH⁺–Ar and PhOH⁺ mass channels at the (a) $\text{IE}_0(\pi)$, (b) β_x^1 , (c) β_y^1 , (d) β_x^2 , and (e) σ_z^1 levels, respectively.