

PHOTODISSOCIATION SPECTROSCOPY OF BARE AND HYDRATED PERMANGANATE IONS

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We report electronic spectra of mass-selected MnO_4^- and $\text{MnO}_4^- \cdot \text{H}_2\text{O}$ using electronic photodissociation spectroscopy. Upon photoabsorption, bare MnO_4^- ions decay by formation of MnO_3^- and MnO_2^- . In contrast, hydrated permanganate predominantly fragments by loss of the water molecule. The 1^1T_2 band in the visible spectral region shows a well-resolved vibrational progression consistent with the excitation of a Mn-O stretching mode. Weaker vibrational signatures are also observed in the much broader UV absorption bands. The presence of a single water molecule does not perturb the spectrum of MnO_4^- except for a very small blue shift, while full hydration (i.e. in aqueous solution) leads to a blue shift of up to 800 cm^{-1} . The experimental data can be used as benchmarks for electronic structure theory methods, which usually predict electronic spectra *in vacuo*.