PHOTODISSOCIATION SPECTROSCOPY OF BARE AND HYDRATED PERMANGANATE IONS

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We report electronic spectra of mass-selected $MnO_4^-$ and $MnO_4^- \cdot H_2O$ 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*.