WATER ON THE SUN: A NEW SPECTROSCOPIC PARADIGM

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Sunspot infrared absorption spectra with $T \sim 3000°$ C and $750 \leq \tilde{\nu} \leq 1010$ cm^{-1} have recently been reported[a]. The spectra are highly congested (~ 50 lines per cm^{-1}) with spectral lines thought to be due to water. Traditional perturbation theory is inadequate for analysing this problem. Instead we employ full variational solutions of the problem which go beyond the standard Born-Oppenheimer approximation. This treatment leads to vibration-rotation quantum number assignments for individual lines (none of which had been previously assigned). Furthermore we attribute many more spectral lines to water than could be achieved using previous theory or experiment[a]. In particular we assign transitions involving rotational levels in the ground state and first few vibrational states up to 22,000 cm^{-1} above the ground state, about double that previously known and approximately halfway to dissociation. In addition we assign levels with K_a as high as 32 compared to the previous maximum of 20. We find previously unobserved and unanticipated spectroscopic characteristics of water. These characteristics will be present in other hot water spectra found in flames, rocket plumes, cool stellar atmospheres and elsewhere, as well as in the spectra of other hot molecules. The approach applied here thus represents a paradigm shift in the theory of polyatomic molecular spectroscopy which we expect will be widely followed in all future treatments of the spectra of hot molecules.

[a] L. Wallace, *et al Science* **268**, 1155-1158 (1995).