SPECTROSCOPIC CHARACTERIZATION OF THE OH(A)-Xe BOND IN THE GAS PHASE AND IN CRYOGENIC MATRICES

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Electronic spectra for matrix isolated OH show red-shifted emission bands, indicating that the $A\,^2\Sigma^+$ state interacts with rare gas atoms more strongly than the $X\,^2\Pi$ ground state. For the rare gases Ne, Ar and Kr the excited state interactions are consistent with the formation of moderate to strong van der Waals bonds. Studies of the binary OH-Rg complexes in the gas phase confirm this interpretation.

Spectra for OH trapped in a Xe matrix or OH-Xe in solid Ar are markedly different from those obtained with the other rare gases. Here the spectra indicate the formation of an incipient chemical bond between OH(A) and Xe. For example, the A-X emission spectrum is red-shifted by 8100 cm^{-1} relative to that of OH in the gas phase. In the present work we have re-examined the matrix spectrum of OH-Xe, and characterized the binary complex in the gas phase for the first time. The spectra for the complex were barely shifted from the transition of free OH, and showed vibrational spacings for the intermolecular stretch that were consistent with a weak van der Waals interaction. In both the matrix and the gas phase, OH(A)-Xe exhibits a fluorescence decay rate that is much faster than the OH(A) radiative decay rate.

In this talk the spectroscopic data will be presented and a model that resolves the apparent conflict between the matrix and gas phase results will be discussed.