SUBSTITUENT EFFECTS IN THE O-H VIBRATIONAL INTENSITIES OF VAPOR PHASE ALCOHOLS AND ACIDS

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We have measured integrated intensities of O-H stretching bands, both fundamentals and overtones, for a wide variety of vapor phase alcohol and acid species. In turn, we have identified several specific trends in the data that parallel the inductive nature of the adjacent substituent. While fundamental intensities clearly increase with the electronegativity of the substituent, directly analogous trends for overtones are less apparent. However, substituent electronegativity does parallel overtone intensity fall-off, which refers to the proportional decrease in overtone intensity, relative to that of the fundamental. We have attempted to model the intensities a two-parameter, linear-exponential dipole moment function, but the agreement between observed and calculated intensities is only fair. In any event, the overall shapes of these functions also parallel substituent electronegativity, and offer some tentative rationale for the observed intensity trends. Very recently we have attempted to solidify this rationale through an examination of ab initio dipole moment functions. We have also undertaken an investigation of solvent effects on the O-H vibrational bands of n-propanol, and these recent results will also be discussed.