SPECTROSCOPIC IMPLICATIONS OF THE COUPLING OF UNQUENCHED ELECTRONIC ANGULAR MOMENTUM TO ROTATION IN THE OH–ACETYLENE COMPLEX

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A model is developed for the rotational energy levels and transition intensities of non-linear OH-containing complexes in which the OH is hydrogen bonded to its partner. Both the A' and A'' electronic states arising from the lifting of the OH monomer electronic orbital degeneracy are explicitly included. Consequently, the model smoothly spans the entire range of the difference potential responsible for the separation between these two states and accounts for the partial quenching of the OH monomer electronic angular momentum in such complexes. The more familiar cases of completely unquenched and completely quenched electronic angular momentum are recovered in the limits of zero and very large difference potential, respectively. The sensitivity of vibration-rotational spectra to the value of the difference potential is investigated for a-type and b-type transitions, and it is shown that spectra of reactant complexes will reveal the extent of quenching that must occur along the reaction coordinate from weakly interacting partners to addition product. The model is successfully applied to the analysis of the observed infrared bands of the OH–acetylene complex and allows the determination of the A rotational constant and difference potential from the b-type, C-H stretching band.