THEORETICAL STUDIES OF HIGHLY EXCITED VIBRATIONAL STATES USING VAN VLECK PERTURBATION THEORY

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While there are now many powerful theoretical approaches for calculating the nature of highly excited states of small molecules, Van Vleck perturbation theory remains an important and competitive tool for the interpretation of molecular spectra. Several molecular examples, including CH_3OH, CH_4, H_2CO, HFCO, $SCCl_2$, and CHF_3, are described in order illustrate this point. Combining Van Vleck perturbation theory with variational methods or semiclassical analysis enables one to extend the range of traditional perturbation theories. Our work in this area is described. With the former, both torsional splittings tunneling in methanol and the multiple time scales of vibrational decay in the $v = 4 - 5$ CH stretch overtones of fluoroform have been calculated. With the latter, eigenstates for $SCCl_2$ have been assigned in a region with multiple Fermi resonance interactions.