LOCAL MODE EFFECTS ON VIBRATIONAL AND ROTATIONAL ENERGY LEVEL PATTERNS IN SMALL SYMMETRICAL MOLECULES

L. HALONEN, *Laboratory of Physical Chemistry, P. O. Box 55 (A. I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland.*

Simple curvilinear internal coordinate vibrational Hamiltonians obtained from exact theory are used to construct local mode models including both stretching and bending vibrations in XH_2, XH_3, and XH_4 type molecules. The models which include local mode harmonic couplings between stretching oscillators and Fermi resonance couplings between stretches and bends are defined through matrix elements. Unitary transformations are found to provide a link between the local mode and the traditional normal mode pictures. Extensions of the theory to the rotational motion of highly excited stretching states show the dynamical change of symmetry, i. e., for example in XH_3 from C_{3v} to C_s. The implications of these kind of effects on effective rotational Hamiltonians are discussed.