THE CALCULATION OF ROTATIONAL ENERGY LEVELS USING TUNNELING HAMILTONIANS

JON T. HOUGEN, *Optical Technology Division, NIST, Gaithersburg, MD 20899-8441*.

The present talk will present a pedagogical introduction and review of 25 years of using tunneling Hamiltonians to parameterize and fit rotationally resolved spectra of small polyatomic molecules with one or more large-amplitude motions (LAMs). This tunneling formalism does not require a quantitative knowledge of the potential surface, but instead makes use only of its symmetry properties. Topics planned for discussion include: the user communities for such Hamiltonians; the range of applicability and achievable accuracy; a representative list of molecules treated to date and their various combinations of internal-rotation, inversion, hydrogen-bond-exchange, and H-atom-transfer LAMs; a way of organizing the LAMs of these molecules in the mind using the piston-and-crankshaft vocabulary of the reciprocating engine; how the theoretical tools of point-groups, permutation-inversion groups, extended groups, and time reversal are used in the tunneling-Hamiltonian formalism; and finally a brief report on the present status of two unfinished applications of the tunneling-Hamiltonian formalism, namely cis/trans bent acetylene (HCCH) and protonated acetylene ($C_2H_3^+$).