GLOBAL CALCULATIONS USING POTENTIAL FUNCTIONS AND EFFECTIVE HAMILTONIAN MODELS FOR VIBRATION-ROTATION SPECTROSCOPY AND DYNAMICS OF SMALL POLYATOMIC MOLECULES

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It has become increasingly common to use accurate potential energy surfaces and dipole moment surfaces for predictions and assignment of high-resolution vibration-rotation molecular spectra. These surfaces are obtained either from high-level $ab\ initio$ electronic structure calculations or from a direct fit to experimental spectroscopic data. The talk will continue a discussion of some recent advances in the domain of the "potentiology". The role of basis extrapolations, of the Born-Oppenheimer breakdown corrections , in particular for very highly excited vibration states will be considered. As effective polyad Hamiltonians and band transition moment operators are still widely used for data reductions in high-resolutions molecular spectroscopy, experimental spectra analyses invoke a need for accurate methods of building physically meaningful effective models from $ab\ initio$ surfaces. This involves predictions for various spectroscopic constants, including vibration dependence of rotational and centrifugal distortion and resonance coupling parameters. Topics planned for discussion include: high-order Contact Transformations of rovibrational Hamiltonians and of the dipole moment for small polyatomic molecules; convergence issues; the role of the anharmonicity in a potential energy function and of resonance couplings on the normal mode mixing and on vib-rot assignments with application to high energy vibration levels of SO_2 and to ozone near the dissociation limit; intensity anomalies in H_2S / HDS / D_2S spectra, relation of the shape of $ab\ initio$ dipole moment surfaces with a "mystery" of nearly vanishing symmetry allowed bands. A full account for symmetry properties requires efficient theoretical tools for transformations of molecular Hamiltonians such as irreducible tensor formalism, applications using phosphine and methane potentials will be discussed. Both potential functions and effective polyad Hamiltonians allow studying changes in quasi-classical vibration periodic orbits and in of the nodal structure of wavefunctions with mass variations. An investigation of the consequences of symmetry breaking by isotopic substitution, in the classical and quantum dynamics is particularly instructive. This helps understanding the fingerprints of bifurcations effects in the quantum states of isotopologues and their assignment. The work of our research team with collaborators in these areas will be described.