THE EXCEL-ERATION OF METHANOL SPECTROSCOPY: ISOTOPIC TUNING OF TORSION-VIBRATION INTERACTIONS

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One of the current "frontiers" in the spectroscopy of molecules with large amplitude motion is the extension of the analysis of excited vibrational states to move beyond the isolated state model to a more global treatment including several coupled vibrational modes. Before that, of course, one needs to explore the isolated states themselves, and there are still states even for small molecules like methanol, methyl mercaptan and methylamine whose structures have not yet been characterized in detail. In this task, the use of Loomis-Wood plots and Excel spreadsheets has proved to be very helpful, in conjunction with solid bases of ground-state energy term values provided by the pioneering work of the microwave and THz community. The Excel difference table approach relies on systematic trends in the J-dependence of the spectral sub-bands, and can be a sensitive pointer to perturbations arising from level-crossing resonances between interacting modes. The vibrational modes can also exhibit anharmonic resonances with the ground-state torsional manifold as it rises up through the vibrational regions. Isotopic substitution can then serve as a useful tool for tuning the resonances with two degrees of freedom, one along the energy axis by altering the relative energies of the coupled states, and a second along the K-axis by changing the value of the ρ parameter which governs the periodic K-dependence of the torsional energies. Examples will be presented of this "isotopic tuning" for isotopologues of methanol, along with discussion of features of the Excel spreadsheet approach. We will also illustrate how isotopic shifts may give insight into sub-band vibrational assignments from comparison of the torsion-vibration manifolds of the lower modes of normal CH_3OH and its O-18 relative.