CORRELATION PROBLEMS AND CORRELATION-FREE TORSION ROTATION HAMILTONIAN FOR A MOLECULAR WITH AN INTERNAL ROTOR

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Motivated by investigating how to develop a correlation-free reduced form of torsion-rotation Hamiltonian that is rapid convergent and suitiable for analyzing observed spectra for methanol and its isotopic species, the origin of various classes of correlation problems often encountered in fitting the molecular constants to experimental data is analyzed for a molecule with an internal rotation. This analysis will help spectroscopists to overcome certain difficulties in the process of fitting observed spectra. It is showed that the correlation problems can be completely eliminated by considering either the data set or the reduction of Hamiltonian together with practical considerations, where an appropriate definition of order of magnitude is very important. For a molecule with $C_{3v}(M)$ symmetry such as methanol and its isotopic species, it is found that some terms which are included in the traditional or a reduced Hamiltonian given so far shou1d not be used simultaneously. For example, the traditional terms $k_5 P_a^2(1-\cos 3\gamma)$ and $k_6 P_a\{P_\gamma, 1-\cos 3\gamma\}$ should not be used simultaneously, one of three traditional terms $k_6 P_a\{P_\gamma, 1-\cos 3\gamma\}$, $k_7\{P_\gamma^2, 1-\cos 3\gamma\}$, and $\frac{V_6}{2}(1-\cos 6\gamma)$ must be removed, and the term $DD_{ab}P^4\{P_a, P_b\}$ should be removed. In addition, some terms with $\Delta K = \pm 3$ and $\Delta K = \pm 4$ matrix elements should be included in a reduced Hamiltonian. A proposed correlation-free Hamiltonian is tested on analyzing observed data for methanol and its isotopic species.