JIM WATSON AND THE THEORY OF VIBRATION-ROTATION INTERACTION

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Based on the the Coriolis interaction conceived by Teller and Tisza (1932), the fundamental Wilson-Howard Hamiltonian (WHH), formulated in 1936[a], includes everything about the vibration-rotation interaction. Enormous technical advances followed both in vibrational and rotational spectroscopy and have produced extremely rich data. Then God sent us the genius Jim Watson to deeply study the WHH and harvest all its fruits in the most sublime and direct manner.

Out of the many jewels Watson left us I single out three works.

(1) The theory of the centrifugal distortion of asymmetric-top molecules (1966)[b]: To solve the indeterminacy of centrifugal distortion constants of non-planar asymmetric tops, Watson discovered an angular momentum operator $P_x P_y P_z + P_z P_y P_x$ which commutes with the rotational Hamiltonian and produces an additional relation between centrifugal constants making the solutions possible. This is the most frequently quoted paper in the field of molecular spectroscopy.

(2) Simplification of the WHH (1968)[c]: For the first term of rearranged WHH $H = 1/2\Sigma(\Pi_\alpha - \pi_\alpha)\mu_{\alpha\beta}(\Pi_\beta - \pi_\beta)$ Watson discovered commutation relation $[\pi_\alpha, \mu_{\alpha\beta}]=0$. using absolutely beautiful tensor algebra, thus simplifying the Hamiltonian. This is the most fundamental work in the field of molecular spectroscopy and represents the triumph of tensor algebra.

(3) Forbidden rotational transitions (1971)[d]: The $\Delta K=0$ selection rule of a symmetric top molecule corresponds to cylindrical symmetry. Since the actual symmetry is C_3 rather than cylindrical for say NH_3, $\Delta K=3$ forbidden transitions are weakly allowed. Watson's theory showed that non-polar molecules such as CH_4 and H_3^+ are polar in some rotational levels and undergo forbidden rotational transitions. This theory has greatly influenced molecular astrophysics. [e]

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[a] Wilson, Jr., E. B. & Howard, J. B. 1936 J. Chem. Phys. 4, 260

[b] Watson, J. K. G. 1966 J. Chem. Phys. 45, 1360; 46, 1935; 1968 J. Chem. Phys. 48, 4517

[c] Watson, J. K. G. 1968 Mol. Phys. 15, 479

[d] Watson, J. K. G. 1971 J. Mol. Speectrosc. 40, 536

[e] e.g. Oka, T., Geballe, T. R., Goto, M., Usuda, T., McCall, B. J., & Indriolo, N. 2019 ApJ, 883, 54