Joyful Pursuit of Molecular Dynamics and Spectra

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This talk will hark back 60 years, to my graduate student days using microwave spectroscopy, and then look ahead to current prophetic excursions, using intense laser spectroscopy. My Ph.D. mentor, E. Bright Wilson, was a superb scientist and mentor. In the mid-1950s, his lab was focused on rotational spectra perturbed by hindered internal torsion of a methyl group on asymmetric top molecules. A major part of my thesis was devoted to propylene oxide, chosen as ideal to test theory dealing with the three-fold barrier for methyl torsion, which induces tunneling among the rotational levels. With Jerry Swalen, we measured spectra over a very large range of rotational lines (J = 1 to 48, K = 1–25) and found dramatic splittings due to tunneling, confirming theory.

Another happy episode dealt with the equilibrium conformation of propylene. With Larry Krisher, we were curious whether one of the methyl hydrogens is eclipsed with respect to the double bond. To find out, we had fun making a sample of $CH_2DCH{=}CH_2$. In just a few hours, we had confirmed the expected two distinct rotational isomers: one had D eclipse the double bond, the other had D staggered. Thirty years later, I was astonished by a talk by Yoshi Kishi. He reported an epic synthesis of palytoxin, $C_{129}H_{223}N_3O_{54}$, a molecule with $2^{72} = 5 \times 10^{21}$ distinct stereoisomers. Kishi achieved, in 8-years, the exact stereoisomer he wanted—the biologically active neurotoxin. He had devised a key steric tool, by knowing the propylene conformation.

This month, with Qi Wei, Sabre Kais, and Tomokazu Yasuike, we have sent off a theoretical paper titled "Molecular binding induced by intense laser fields: helium dimer, pendular states, and strong chemical bonds." We treat two pulsed laser realms: (I) Fields not strong enough to dislodge electrons, but interact with the anisotropic *polarizability* to induce spatial alignment of the molecular axis. (II) Superintense, high-frequency lasers that impel electrons to undergo *quiver oscillations* which interact with the intrinsic Coulomb forces and induce an extremely strong chemical bond. By including in (II) an excited electronic state, we bring out features amenable to experimental spectroscopy.