THE INTRIGUING $F_{bc}(P_bP_c+P_cP_b)$ TERM IN THE INTERACTION HAMILTONIAN FOR TUNNELING BETWEEN EQUIVALENT GAUCHE CONFORMERS

PETER GRONER, *Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA*.

This study was triggered by the results of the microwave investigation of triflic acid (TA), $CF_3 - SO_2 - OH$, and its deuterated (TA-d) and ^{34}S (TA-S) isotopologues by Huff et al.[a] To fit the observed transitions split by gauche-gauche tunneling due to the CS-OH internal rotation, the interaction Hamiltonians for TA and TA-S required the term $F_{bc}(P_bP_c + P_cP_b)$. In contrast, the Coriolis term g_aP_a had to be used for TA-d.

The F_{bc} term results from two facts: 1) The moment of inertia tensor I and its inverse, the μ-tensor, of both the right- and left-handed forms of the gauche conformers need to be expressed in the same molecule-fixed axis system; 2) The Cartesian coordinates of some or all atoms and the components of I depend on the internal rotation coordinate τ. If we define a Cartesian axis system with two of the axes in the symmetry plane of the transition state between the two conformers, the third axis is perpendicular to it. When τ changes, the moving atoms will eventually cross the symmetry plane and their 3rd Cartesian coordinate will change its sign and with it also the signs of two off-diagonal components of I and the μ-tensors.

The rotational Hamiltonian in a 2-by-2 block format contains the contributions of the right and left gauche conformers (H_R and H_L, respectively) on the diagonal and the Coriolis interactions in the off-diagonal blocks. If the internal rotation wave functions ϕ_R and ϕ_L are symmetrized to $\phi_{A'}$ and $\phi_{A''}$ to conform with C_s symmetry, the diagonal blocks of the Hamiltonian become $H_{A'}$ and $H_{A''}$. The off-diagonal blocks contain now the Coriolis terms and the contributions from the sign-changing μ-tensor components.

Detailed explanations and a demonstration that this particular interaction may be especially important for $K_a = 1$ energy levels will be presented.

[a] A.K. Huff, N. Love, C.J. Smith, K.R. Leopold, (2022) submitted for publication.