

VARIATION OF CH STRETCH FREQUENCIES WITH CH₄ ORIENTATION IN THE CH₄ – F⁻ COMPLEX: MULTIPLE RESONANCES AS VIBRATIONAL CONICAL INTERSECTIONS

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In the CH₄ – F⁻ complex, an adiabatic separation of the CH stretch frequencies from the CH₄ orientational coordinates allows the calculation of the four adiabatic CH stretch surfaces. These ab initio calculations reveal (i) a large variation of CH stretch frequencies ($>100\text{ cm}^{-1}$) in the orientational space and (ii) the existence of four symmetrically equivalent sets of vibrational conical intersections (CIs). Two sets of symmetry-allowed CIs are identified in addition to the symmetry-required CIs at the front- and back-side C_{3v} geometries. These results have implications for the evolution of excited CH vibrations in methane during its approach to a potentially reactive surface.