TUNNELING SPLITTINGS IN VIBRONIC STRUCTURE OF CH_3F^+ ($\tilde{X}^2E$): STUDIED BY HIGH RESOLUTION PHOTOELECTRON SPECTRA AND $AB\ INITIO$ THEORETICAL METHOD

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We report a combined experimental and theoretical study on the vibronic structure of CH_3F^+. The results show that the tunneling splittings of vibrational energy levels occur in CH_3F^+ due to the Jahn-Teller effect. Experimentally, we have measured a high resolution ZEKE spectrum of CH_3F up to 3500 cm^{-1} above the ground state. Theoretically, we performed an $ab\ initio$ calculation based on the diabatic model.[a] The adiabatic potential energy surfaces (APES) of CH_3F^+ have been calculated at the MRCI/CAS/avq(t)z level and expressed by Taylor expansions with normal coordinates as variables. The energy gradients for the lower and upper APES, the derivative couplings between them and also the energies of the APES have been used to determine the coefficients in the Taylor expansion.[b] The spin-vibronic energy levels have been calculated by accounting all six vibrational modes and their couplings. The experimental ZEKE spectra were assigned based on the theoretical calculations.

[a] W. Domcke, D. R. Yarkony, and H. Köpple (Eds.), Conical Intersections: Eletronic Structure, Dynamics and Spectroscopy (World Scientific, Singapore, 2004).

[b] M. S. Schuurman, D. E. Weinberg, and D. R. Yarkony, J. Chem. Phys. 127, 104309 (2007).