THE JAHN-TELLER EFFECT IN CH_4^+ : ASSIGNMENT OF THE ROTATIONALLY RESOLVED PHOTOELECTRON SPECTRUM

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The rotationally resolved PFI-ZEKE photoelectron spectrum of methane was first recorded in 1998[a], but its rotational structure has remained unassigned since. These experiments have shown that CH_4^+ possesses a distorted equilibrium geometry of C_{2v} symmetry but is very fluxional in its ground vibronic state.

A new theoretical analysis of the Jahn-Teller effect has been performed which predicts the symmetries and energetics of the vibronic states resulting from large-amplitude pseudorotational dynamics. The ground vibronic state is described as a tunneling doublet with a splitting on the order of the rotational constant. Its rotational structure is described in terms of a simple rotation-tunneling Hamiltonian developped for this purpose.

Combining sources of infrared (IR) and vacuum-ultraviolet (VUV) radiation in two complementary double-resonance experiments has enabled us to assign nuclear spin-symmetries for the lowest rovibronic levels of CH_4^+. Narrow-band infrared radiation at 3.3 μm was generated by difference-frequency-mixing and used to excite selected rovibrational transitions of the antisymmetric stretch vibration. In the first experiment a selected IR transition was saturated and the depletion of PFI-ZEKE photoelectron signal was monitored. In the second experiment photoelectron spectra were recorded from single rotational levels prepared by IR excitation. The results of these experiments will be presented and compared to the theoretical models.

[a] see R. Signorell and F. Merkt, *Faraday Discussions* **115**, 205-228 (2000) and references therein