

INFRARED SPECTRA OF CH_3^+ - Rg_n COMPLEXES (Rg=He,Ne,Ar, n=1,2)

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Rotationally resolved infrared photodissociation spectra of CH_3^+ - Rg_n ionic complexes (Rg=He,Ne,Ar, n=1,2) have been recorded in a tandem mass spectrometer. The spectra of the dimers are compatible with π -bonded equilibrium structures where the Rg atoms are attached to the vacant $2p_z$ orbital of the central C atom (C_{3v} symmetry). In the case of Ar, partial charge transfer into this orbital leads to a large binding energy of the complex (ca. 0.5 eV), so that only overtones of the CH stretch modes can be observed in the photofragmentation spectra. The strong intermolecular bond induces a massive deformation of the CH_3^+ ion which transforms from sp^2 towards sp^3 hybridization. In the Ar- CH_3^+ -Ar trimer the second Ar atom is weakly attached to the other side of the $2p_z$ orbital of C (C_{3v} symmetry). The two C-Ar bonds are not equivalent: one is strong and short, the other one is long and weak. However, tunneling splittings reveal that they can exchange their role via the intracluster inversion motion of CH_3^+ through a transition state with D_{3h} symmetry^a. The intermolecular bonds in the He and Ne containing complexes are much weaker and result mainly from induction interactions. The CH_3^+ deformation is smaller and the absence of the tunneling splittings in the Ne- CH_3^+ -Ne spectrum suggests that the trimers have D_{3h} equilibrium geometries. The experimental results are supported by ab initio calculations.

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