INFRARED SPECTRA OF CH$_3^+$-Rg$_n$ COMPLEXES (Rg=He,Ne,Ah, n=1,2)

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Rotationally resolved infrared photodissociation spectra of CH$_3^+$-Rg$_n$ ionic complexes (Rg=He,Ne,Ah, n=1,2) have been recorded in a tandem mass spectrometer. The spectra of the dimers are compatible with $\pi$-bonded equilibrium structures where the Rg atoms are attached to the vacant 2p$_2$ orbital of the central C atom ($C_{3v}$ symmetry). In the case of Ah, 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$_2$ 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.