DFT studies of H_3N–X (X= Li, Na, K, Rb, Cs and Fr) systems.

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Streszczenie

Complexes of alkali atoms with ammonium have been studied using the Denity Functional Theory with nonlocal and quasi-relativistic corrections. The stable complexes were found for allalkali atom–ammonia complexes. The calculated interaction energies decrease as one progresses down the periodic table and are in range from –18.9 kcal/mol for lithium system up to –6.5 kcal/mol for the frans complex. Similar tendency is noted for the calculated values of charge transfer. The influence of calculated quasi-relativistic (QR) corrections on values of interaction energies is determined. The QR corrections have no effect on lithium complexes whereas reduce the binding energy from 0.1 kcal/mol for Na system up to 0.9 kcal/mol for Fr complex. The DFT calculated IR harmonic frequencies are compared with experimental values and discussed. The calculated vibrational freuencies of ammonia in complexes exhibit trends that for all systems they are parallel to the strength of the bind ing energies. For the H3N–Li complex the vibrational analysis was supported by an harmonic calculations at the MP2 level. It has been shown that there is a discrepancy between the experimental assignment and MP2 harmonic and an harmonic low frequency intermolecular modes.

Słowa kluczowe

density functional methods, MP2 method, molecular complexes, alkali atoms, ammonia, relativistic effects, vibrational frequencies, anharmonic vibrational spectra