

***Ab-initio* study of lithium ion solvation in acetonitrile**

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Keywords: *lithium, acetonitrile, solvation, ab-initio.*

Abstract

Solvation structures and energy characteristics of the lithium ion solvated by acetonitrile molecules were studied by quantum chemical calculations. Formation of the first and the second formation shell is considered. Estimation of calculation accuracy and choosing of basis set were provided. RHF+MP2 level of theory with 6-311G** basis set was chosen to obtain corrected results. It was found that any one of the $\text{Li}^+(\text{CH}_3\text{CN})_n$ ($n = 1-6$) solvates with acetonitrile molecules in the first coordination shell can be formed, but the most probable is $n = 4$. The n value of 6 corresponds to the maximum allowable number of acetonitrile molecules in the first coordination shell of lithium cation. It was established that the formation of the second coordination sphere for Li^+ in acetonitrile is unlikely.

The full IR spectrum for each stable cluster $\text{Li}^+(\text{CH}_3\text{CN})_n$ ($n = 1, 2, 3, 4, 5, 6, 4+2, 6+1$) in a gas phase has been calculated, and new information about the manifestation of solvate geometry in vibrational spectra was obtained. The most characteristic vibrations caused by relative vibrations of Li^+ and coordinated acetonitrile molecules as a whole are located in far-infrared spectral region ($0-700 \text{ cm}^{-1}$). Each stable cluster has specific spectral pattern in this spectral region, which can be used to identify the composition and geometry of the solvates.