VIBRATIONAL PROPERTIES OF X_3^+ AND X_5^+ (X=F, Cl, Br, I) CLUSTERS IN MADELUNG POTENTIALS

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The infrared and Raman spectra of the trihalogen and pentahalogen cations are well known from experiments on crystals containing them as counterions. A proper analysis of the spectra is impossible without taking into account the influence of the crystal field on the cation. In this work, ab initio and density functional calculations have been carried out on the free X_3^+ and X_5^+ (X=F, Cl, Br, I) cluster cations. Comparable calculations have been performed on the clusters Cl_3^+, Br_3^+, I_3^+, Br_5^+, I_5^+, $I_3Cl_2^+$, and $I_3Br_2^+$ embedded in the point charges derived from the Madelung potentials of the crystal fields. It has been shown that the Madelung potential plays an important role in the vibrational properties of these cations with strong cation-anion interactions. The computed vibrational frequencies, force constants, and infrared intensities are in good agreement with the experimental data.