Abstract

This thesis is based on experimental investigations of water cluster ions $H^+(H_2O)_n$ (n = 2 – 6), $D^+(D_2O)_3$ and ammonia cluster ions $X^+(NX_3)_n$ (X = H, D and n = 1 – 3) involved in dissociative recombination (DR). The DR process can be described in a simplified way as a molecular ion capturing a free electron and subsequently dissociating into neutral fragments. The process is of fundamental importance and it plays an important role in ion and radical chemistry in low temperature plasmas with free electrons available, including interstellar clouds, the upper atmosphere of Earth, and man-made plasmas such as electric discharges and rocket and jet exhausts.

The experiments have been carried out at the heavy-ion storage ring CRYRING located at the Manne Siegbahn Laboratory in Stockholm. Absolute DR cross sections have for the first time been measured for most of the studied ions. The cross sections decrease monotonically with increasing energy with an energy dependence close to E^{-1} in the lower part of the energy range and a faster fall-off at higher energies, in agreement with the behavior of other studied heavy ions.

Thermal DR rate coefficients have been determined for the ions in the temperature interval from tens of K up to a few thousand K. The results for water and ammonia-containing ions show similar trends with cluster size. The rate coefficients are in general lower than reported from earlier afterglow experiments, and the water cluster ions show a somewhat different trend with increasing cluster size than earlier studies.

The products from the DR reaction have for the first time been characterized for most of the ions. The DR process results in efficient transfer of energy into internal degrees of freedom, and strong fragmentation is observed for all ions studied. Decomposition is dominated by the channels producing nX_2O + X and nNX_3 + X (X = H, D) for the two cluster ion series. Minor channels are also characterized and isotope effects are described.

Key words: dissociative recombination, ion storage ring, water cluster ions, ammonia cluster ions

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