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First observation of transfer ionization between Ar^+ and Br^-, I^-[1]
THOMAS M. MILLER, NICHOLAS S. SHUMAN, ALBERT A. VIGGIANO, Air Force Research Laboratory, RAINER JOHNSEN, University of Pittsburgh — We have studied reactions between noble gas positive ions and atomic halogen negative ions at thermal energies to determine mutual neutralization rate coefficients. In the cases of $Ar^+ + Br^-$ and $Ar^+ + I^-$, we have observed not only mutual neutralization, but also transfer ionization, e.g., yielding $Ar + Br^+ + e^-$ and $Ar + I^+ + e^-$, respectively. The reactions are exothermic at thermal energies, by 0.58 and 2.25 eV, and rate coefficients of $1.9(\pm 0.6) \times 10^{-9}$ and $1.1(+0.8,-0.3) \times 10^{-9}$ cm^3/s, respectively, were measured at 300 K. Transfer ionization accounts for about 40% of the loss of Ar^+ in reaction with Br^- and 6% in the I^- case, with the remainder being due to mutual neutralization. Measurements at 400 and 500 K indicate a temperature dependence between $T^{-0.5}$ and T^{-1}. In contrast to the Br^- and I^- cases, the transfer ionization reaction between Ar^+ and Cl^- is endothermic by 0.82 eV, and only the neutralization channel is observed. We surmise that an initial electron transfer takes place in the reaction at an avoided curve crossing. That process may result in excited Ar* (perhaps in a 4s state) with enough energy to ionize Br or I.

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