Applications of Molecular Guides to Studying Chemical Reactions

Justin Jankunas, B. Bertsche, K. Reisyan, A. Osterwalder

Institute of Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne 1015, Switzerland

The versatility of molecular guides is demonstrated by steering atomic and molecular beams over a 10º turn. (**i**) In a so-called merged-beam setup chemical reactions can be studied at a vanishingly small nominal relative reactant velocity. In this case, a beam of polar molecules is guided with an electric hexapole and overlapped with a beam of paramagnetic atoms guided by a combination of magnetic hexapole and magnetic quadrupole. Penning ionization reactions between metastable atoms, e.g. He($^3S_1$), and Ne($^3P_2$), and a number of polar molecules, NH_3/ND_3, CH_3F, CHF_3, and C_3HF_3 (3,3,3-trifluoropropyne), have been studied and in some cases integral cross sections measured in the collision energy range from 38 mK (3.3 μeV; 0.026 cm^{-1}) up to 250 K (21 meV; 174 cm^{-1}). Interestingly enough, we find that reaction dynamics of He* + $CHF_3 \rightarrow CF_3^+/CH_2F^+/CHF^+ + e^-$, and Ne* + $CHF_3 \rightarrow CF_3^+/CHF_2^+$ molecular collisions differs dramatically from analogous He* and Ne* reactions with NH_3 and CH_3F molecules. Easy-to-interpret Langevin capture models explain the observed ionization rate of NH_3 and CH_3F molecules by He* and Ne* atoms rather well, whereas the experimentally measured cross section for He* + CHF_3 and Ne* + CHF_3 reactions cannot be reproduced by modified Langevin interaction potential even at a qualitative level. (**ii**) Magnetic hexapole/quadrupole guide has been exploited as an efficient M_J state selector, where M_J is the magnetic quantum number associated with an angular momentum **J**. We find that ground state and metastable atoms with zero nuclear spin, He, C, O, and Ne, emerge from the magnetic guide with their total electronic angular momentum polarized; atoms with hyperfine structure, like N($^4S_{3/2}$), are almost completely depolarized. Application of an external magnetic field ~ 18 cm away from the magnetic quadrupole serves as a quantization axis for paramagnetic atoms. Crossing of Ne($^3P_2$) or He($^3S_1$) atomic beams at 90º with a supersonic expansion of Ar, Kr, CO, or N_2 allowed us to unravel the reactivity of individual M_J sublevels, most notably those associated with $J = 2$ angular momentum in Ne($^3P_2$) atoms. In the case of a Ne($^3P_2$) + Ar molecular collision, we find that $NeAr^+$ associative ionization products are favored over Ne + Ar^+ reaction outcome by a factor of 2.0 ± 0.1 when Ne($^3P_2$) atoms occupy the $M_J = 2$ sublevel compared to $M_J = 0,1$ states. Experimental findings are in a good qualitative agreement with theoretical computations, wherein $M_J = 2$ substates of neon are more reactive than $M_J = 0,1$ levels by a factor of ~ 1.5.