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Electron attachment to fluorocarbon radicals

NICHOLAS SHUMAN, Air Force Research Laboratory

Most plasma environments contain populations of short-lived species such as radicals, the chemistry of which can have significant effects on the overall chemistry of the system. However, few experimental measurements of the kinetics of electron attachment to radicals exist due to the inherent difficulties of working with transient species. Calculations from first principles have been attempted, but are arduous and, because electron attachment is so sensitive to the specifics of the potential surface, their accuracy has not been established. Electron attachment to small fluorocarbon radicals is particularly important, as the data are needed for predictive modeling of plasma etching of semiconductor materials, a key process in the industrial fabrication of microelectronics. We have recently developed a novel flowing afterglow technique to measure several types of otherwise difficult to study plasma processes, including thermal electron attachment to radicals. Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS) exploits dissociative electron attachment in a weakly ionized plasma as a radical source. Here, we apply VENDAMS to a series of halofluorocarbon precursors in order to measure the kinetics of thermal electron attachment to fluorocarbon radicals. Results are presented for CF_2, CF_3, C_2F_5, C_2F_3, 1-C_3F_7, 2-C_3F_7, and C_3F_5 from 300 K to 900 K. Both the magnitude and the temperature dependences of rate coefficients as well as product branching between associative and dissociative attachment are highly system specific; however, thermal attachment to all species is inefficient, never exceeding 5% of the collision rate. The data are analyzed using a recently developed kinetic modeling approach, which uses extended Vogt-Wannier theory as a starting point, accounts for dynamic effects such as coupling between the electron and nuclear motions through empirically validated functional forms, and finally uses statistical theory to determine the fate of the highly excited anion intermediate formed during attachment. The kinetic modeling, along with complimentary data from electron beam measurements, is used to extrapolate the electron attachment rate coefficients to temperature and pressure regimes inaccessible to the experiment, including to non-thermal plasma conditions most relevant to plasma etching.