PULSED JET DISCHARGE MATRIX ISOLATION STUDIES OF RADICALS, IONS, AND WEAKLY BOUND RADICAL-MOLECULE COMPLEXES

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We have recently implemented pulsed jet discharge matrix isolation spectroscopy, a versatile method for trapping and spectroscopic interrogation of reactive intermediates, which combines matrix isolation techniques with a pulsed DC discharge nozzle. This method was initially demonstrated by Bondybey and co-workers,[a] who showed that a variety of transient species (radicals, carbocations, and carbanions) could be trapped. A primary advantage of the pulsed discharge method over continuous deposition is that the short (ms) pulses produce a self-annealing effect due to the instantaneous temperature rise in the surface layers during deposition, which gives rise to clear, highly transparent matrices. We will demonstrate another advantage, in that the dependence of the absorption intensity on discharge current varies dramatically for different species, which provides a convenient diagnostic for spectral identification. By working at discharge currents near threshold, one successfully avoids extensive atomization and fragmentation. Our initial studies of halomethyl radicals, halocarbenium ions, and weakly bound complexes involving the hydroxyl radical trapped in Ar and Ne matrices will be presented. Our results on the halocarbenium ions suggest that the primary mechanism for ion formation is ionization/fragmentation of the precursor induced by collision with metastable rare gas atoms. We will discuss planned modifications to the method that should further broaden its scope and utility.

[a] A. Thoma, B. E. Wurfel, R. Schlachta, G. M. Lask, and V. E. Bondybey, J. Phys. Chem. 1992, 96, 7231-35.