MICROSOLVATION AND PHOTODYNAMICS IN FORMIC ACID-WATER CLUSTERS

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Formic acid is the simplest carboxylic acid and plays a pivotal role in atmospheric chemistry. It is an intermediate in the Water-Gas-Shift reaction, decomposing into either CO_2 and H_2 or into H_2O and CO under ionizing radiation. Furthermore, it is important in acid rain and seeding the nucleation of water molecules in cloud formation. Here, I will present our recent work, where femtosecond lasers are applied to study the microsolvation and photodynamics of molecular gas-phase formic acid-water clusters using time-of-flight mass spectrometry. Our cluster distribution confirms the enhanced stability of $(FA)_5(H2O)_1H^+$, where the formic acid cluster forms a cage-like structure surrounding the water molecule. Upon exposure to high laser intensities (400 nm, 200 fs, laser intensities of 1.9x10^{15} W/cm^2), the clusters undergo an enhanced ionization which produces multiply charged ions of C, O, and CO. Coulomb explosion of these ions leads to a large kinetic energy release that is shown to increase with the size of clusters. The measured values are in agreement with a Molecular Dynamics simulation of the Coulomb explosion for the mean size of the clusters within the cluster distribution, suggesting that no movement occurs during ionization. Of particular relevance, we record a large amount of signal for the carbon monoxide trication. KER values were recorded as high as 44 eV for CO^{3+} for $(FA)_2$, but increases to 75.3 eV when the cluster distribution is shifted toward $(FA)_5$ as the largest signal. Potential energy curves for CO^{3+} are calculated using the multireference configuration interaction (MRCI+Q) method to confirm the existence of metastable states with a large potential barrier with respect to dissociation. This combined experimental and theoretical effort confirms the existence of metastable CO^{3+}.