A QUANTUM CHEMICAL INVESTIGATION OF THE STABILITY AND CHEMISTRY OF THE ANIONS OF CO AND H_2CO IN ASTROPHYSICAL ICES

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Electrons may either be deposited on interstellar icy grain mantles from the gas phase, or they may be produced *in situ* via photoionization. It is energetically favorable for electrons to bind to species in the ice to form anions. Similarly, anions may be formed within icy grain mantles from chemical processes such as proton transfer from an acid to a base. To understand the fate of electrons in astrophysical ices and the potential impact of anions on gas-grain chemistry, we explored the behavior of two common and important interstellar molecules – CO and formaldehyde (H_2CO) – when they interact with an electron in ice. Neither CO nor H_2CO bind an electron in the gas phase. In astrophysical ices, however, quantum chemical calculations indicate that the anions of CO and H_2CO are stabilized by interacting with the polarized field provided by water ice and are bound with respect to CO and H_2CO. We then investigated whether CO^- and H_2CO^- are stable with respect to subsequent chemical reactions and sought to identify vibrational spectroscopic features that might be useful for experimentalists to identify these anions in the laboratory. In our theoretical investigations reported here, we studied CO^- + nH_2O and H_2CO^- + mH_2O in clusters containing from 2 to 17 water molecules using B3LYP/6-31+G** and MP2/6-31+G** calculations. The calculations show that in smaller water clusters, both CO^- and H_2CO^- are stabilized by water molecules. However, in larger clusters, both anions can undergo barrierless reactions in which a proton is transferred from a nearby water molecule, forming radicals such as HCO or H_2COH and hydroxide anion (OH^-). Since HCO and H_2COH are precursors to H_2CO and CH_3OH, electron-induced anion chemistry in ices may contribute to the observed abundances of important astromolecules. In addition to the structures and energetics of these clusters, we will also provide theoretical predictions of spectroscopic features that might be detected in the laboratory or interstellar medium.