

# Formation of Intermolecular Covalent Bonds Observed with IR Photodissociation Spectroscopy

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## ABSTRACT

The formation of covalent bonds between ions and molecules is a primary process in a variety of chemical reactions such as nucleophilic substitution/addition and ion polymerization reactions. In this study, we have observed the intermolecular bond formation in cluster ions of  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{OCS}$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ , methanol, and acetone with IR photodissociation (IRPD) spectroscopy in the  $1000\text{--}4000\text{ cm}^{-1}$  region. In the  $(\text{CO}_2)_n^+$  cluster ions, a covalent bond is formed between  $\text{CO}_2^+$  and  $\text{CO}_2$ , and this structure is retained in larger size clusters; there is a  $\text{C}_2\text{O}_4^+$  dimer ion core, and the other  $\text{CO}_2$  components are solvated to the ion core. The dimer ion core structure is found also for the homo-cluster ions of  $(\text{CS}_2)_n^+$ ,  $(\text{OCS})_n^+$ ,  $(\text{N}_2\text{O})_n^+$ , and  $(\text{acetone})_n^+$ . The introduction of one  $\text{H}_2\text{O}$  molecule to the  $(\text{CO}_2)_n^+$  and  $(\text{N}_2\text{O})_n^+$  cluster ions drastically changes the characteristics of the intermolecular bond. In the  $[\text{H}_2\text{O}(\text{CO}_2)_n]^+$  clusters, the positive charge is localized on the  $\text{H}_2\text{O}$  component, and the  $\text{CO}_2$  molecules are bonded to the  $\text{H}_2\text{O}^+$  ion electrostatically. On the contrary, the  $[\text{H}_2\text{O}(\text{N}_2\text{O})_n]^+$  ions show the formation of a covalent bond between the oxygen atoms of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$ , producing the  $[\text{H}_2\text{O}\text{--}\text{ON}_2]^+$  ion. For the hetero-cluster ions of  $\text{CS}_2$  and  $\text{OCS}$ , the intermolecular covalent bond is also formed between the two  $\text{OCS}$  and one  $\text{CS}_2$  molecules, and the positive charge is delocalized over the three molecules.