

Summary

These studies show that (1) the geometries and charges on atoms of RCOO^- ($\text{R} = \text{H}, \text{CH}_3$ and F), CH_3O^- , CH_3NH_3^+ and CH_3OH_2^+ in aqueous solution are considerably different from those in the gas phase (Table 1). It is the primary cause of those differences that the contributions of resonance structures, $\text{R}^-\dots\text{CO}_2$, $\text{H}^-\dots\text{CH}_2=\text{O}$, $\text{CH}_3^+\dots\text{NH}_3$ and $\text{CH}_3^+\dots\text{OH}_2$, to those ions in aqueous solution are smaller than those in the gas phase. The N-H bond lengths of CH_3NH_3^+ and the O-H bond lengths of CH_3OH_2^+ in aqueous solution are longer than those in the gas phase because water molecules have a great attraction for H in the N-H and O-H bonds, and (2) the geometries of CH_3S^- , CH_3PH_3^+ and CH_3SH_2^+ (except for the S-H bond lengths) in aqueous solution are almost equal to those in the gas phase (Table 1). This means that the contributions of resonance structures, $\text{H}^-\dots\text{CH}_2=\text{S}$, $\text{CH}_3^+\dots\text{PH}_3$ and $\text{CH}_3^+\dots\text{SH}_2$, to these ions in aqueous solution are almost equal to those in the gas phase.

Table 1

The differences between the bond lengths in aqueous solution and those in the gas phase (in Å)

	H-C	C-O
HCOO ⁻	-0.017	+0.004
	C-C	C-O
CH ₃ COO ⁻	-0.022	+0.005
	F-C	C-O
FCOO ⁻	-0.089	+0.011
	C-O	C-H
CH ₃ O ⁻	over 0.044	below -0.024
	C-S	C-H
CH ₃ S ⁻	very small	very small
	C-N	N-H
CH ₃ NH ₃ ⁺	-0.031	+0.018
	C-P	P-H
CH ₃ PH ₃ ⁺	very small	very small
	C-O	O-H
CH ₃ OH ₂ ⁺	below -0.060	over 0.082
	C-S	S-H
CH ₃ SH ₂ ⁺	very small	over 0.040