

## IRMPD SPECTROSCOPY OF $\text{CO}_3^- (\text{H}_2\text{O})_{1,2}$ AND $\text{CO}_4^- (\text{H}_2\text{O})_{1,2}$

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The hydrated radical anions  $\text{CO}_3^- (\text{H}_2\text{O})_{1,2}$  and  $\text{CO}_4^- (\text{H}_2\text{O})_{1,2}$  are important anions in the atmosphere. Quantitative models predict the steady state fractional abundance of  $\text{CO}_3^- (\text{H}_2\text{O})_{0,1}$  to be in the range of 0.3–2.3 % of the total negative ion inventory, with  $\text{CO}_3^- (\text{H}_2\text{O})$  being predicted to be dominating up to an altitude of 11 km [1]. Direct sampling of ions in the boreal forest confirmed the presence of  $\text{CO}_3^- (\text{H}_2\text{O})_{0,1}$  [2]. The  $\text{CO}_4^-$  ion is another radical anion that is derived from  $\text{CO}_2$  and found with a fractional abundance of about 0.01 % [2]. The reactivity often depends strongly on the number of solvating water molecules [3], and therefore the hydration structure is key to understand their reactivity. Infrared multiphoton dissociation (IRMPD) spectroscopy is an excellent tool to collect information on the structure of ions. The spectra were measured in both the C-O and O-H stretch region at ion trap temperatures of 295 K and approx. 80 K [4]. The O-H stretching region exhibits broad spectra with additional maxima and shoulders beside the free O-H stretch frequency for all ions. Clear absorptions are observed in the C-O stretching region, but dissociation of  $\text{CO}_3^- (\text{H}_2\text{O})_{1,2}$  was surprisingly inefficient, probably due to radiative cooling. While  $\text{CO}_3^- (\text{H}_2\text{O})_{1,2}$  and  $\text{CO}_4^- (\text{H}_2\text{O})$  lose water upon dissociation,  $\text{CO}_4^- (\text{H}_2\text{O})_2$  exhibits an additional dissociation channel with loss of  $\text{CO}_2$ . All experimentally measured infrared spectra are compared to calculated spectra within harmonic approximation and from analysis of molecular dynamics (MD) simulations. The comparison of experiment and theory indicates that multiple isomers contribute to the observed spectrum at finite temperatures.

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[3] C. van der Linde et al., *Phys. Chem. Chem. Phys.* 20 (2018) 10838.

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