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Aqueous-phase behavior of glyoxal and methylglyoxal observed with carbon and oxygen K-edge X-ray absorption spectroscopy

Georgia Michailoudi et al.

Correspondence to: Nønne L. Prisle (nonne.prisle@oulu.fi)

S1 Aqueous solutions of glyoxal

The absorption edges of the recorded spectra are presented in Table S1. The absorption energies of different solutions differ by 0.1–0.2 eV, which is just within the photon energy resolution of the measured spectra. We observe that there is a trend to increase the absorption edge energy upon addition of salt or decrease in concentration.

Table S1. Absorption edge of aqueous solutions of pure glyoxal and their mixtures with inorganic salts. Error bars are estimated to be ± 0.1 eV.

Aqueous solution	Absorption edge [eV]
0.5 M $C_2H_2O_2$	289.6
0.5 M $C_2H_2O_2$ + 2 M Na_2SO_4	289.7
0.5 M $C_2H_2O_2$ + 2 M NaCl	289.7
1 M $C_2H_2O_2$	289.5
2 M $C_2H_2O_2$	289.5
2 M $C_2H_2O_2$ + 2 M Na_2SO_4	289.6
2 M $C_2H_2O_2$ + 2 M NaCl	289.6

S2 Gas-phase measurements

We measured gas phase C K-edge XAS spectrum of glyoxal and methylglyoxal, to identify the possible features on the spectra that are related to their unhydrated forms. Each organic compound was initially in aqueous solution, as it was purchased (description of the samples in Sect. 2.1), and was bubbled by helium gas with the pressure of 0.3 MPa, in room temperature (around 25 °C). The formed vapors were flowed in the helium buffer region at room temperature and with helium pressure around 0.1 MPa. The flow rate of the vapors was controlled by the helium gas stream and the flow rate of both the vapors and the helium gas was 190 $\mathrm{cc/min}$ (180 $\mathrm{cc/min}$ for He mixed with sample and 10 cc/min for He gas). The spectra of gas phase glyoxal and methylgyoxal are presented in Fig. S1.

S2.1 Glyoxal

In the gas phase spectrum of glyoxal, we observe a rather intense shoulder at 288.7 eV and a feature dominating at energies above 289.6 eV. The shoulder at 288.7 eV is not observed in the aqueous solution of glyoxal (Fig. 3). This energy is much higher than the one of aldehydic carbonyl predicted by our quantum chemical calculations at 286.18 eV (Table 3) and is closer to the absorption energy of the carboxylic group, assigned in the energy range of 288.2–289 eV (Latham et al., 2017; Tivanski et al., 2007; Russell et al., 2002), indicating possible presence of acid (as CHOCOOH, $\sim$ 2% according to manufacturer Wako) impurities in the solution. There is no distinct peak for C=O, as we would have expected for the pure compound, revealing that during the collection of the unhydrated gas phase glyoxal, vapors of hydrated forms and oligomers might also have evaporated and characterized. The feature at 289.6 eV is also observed in the spectra of aqueous solutions of glyoxal and is related to the ionization threshold and excitations to other unoccupied orbitals.

S2.2 Methylglyoxal

In the case of methylglyoxal, we observe a strong peak at around 288.7 eV (Fig. S1) and a wide feature starting at approximately 289.4 eV. The peak at 288.7 eV is not present in the spectra of the aqueous solutions of methylglyoxal (Fig. 4), while C 1s $\rightarrow \pi^*$ (C=O) excitations around 286 eV (calculated at 286.23–287.05 eV) are not observed in the gas phase spectra. Similarly to the case of glyoxal, we may consider possible contributions from by-products and/or photodecomposition. The broader feature at 289.4 eV can be related to transitions of the C-OH groups of the hydrates.

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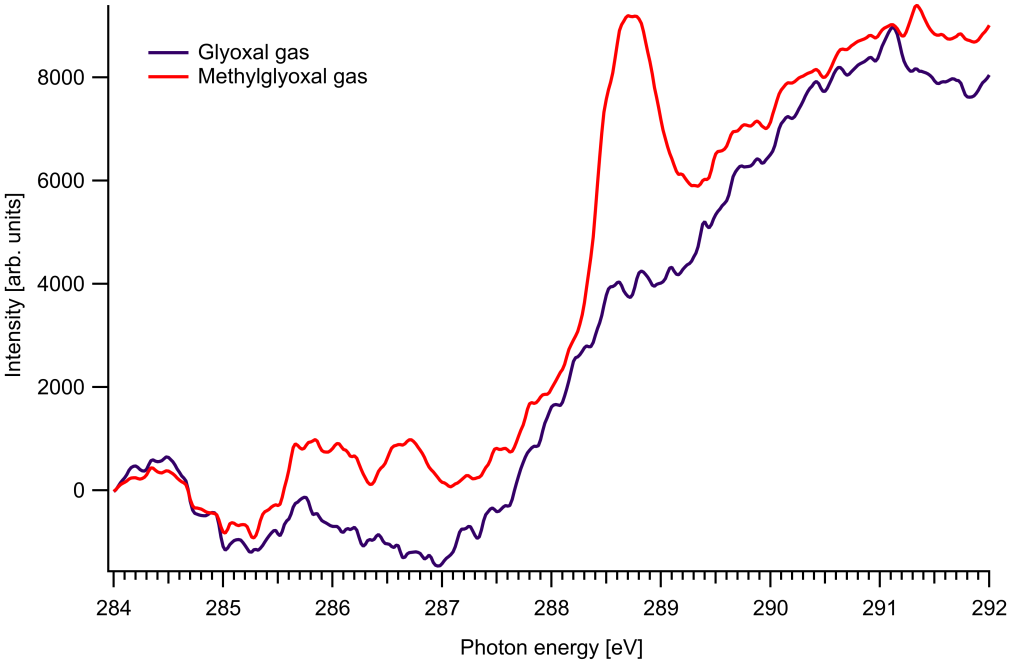

Figure S1. C K-edge spectra of glyoxal and methylglyoxal in gas phase.