Point 1:

Understanding how atoms or molecules respond to irradiation with x-rays gives insight into the structure of solutions (Ref. 1 and references therein), and the mechanisms of radiation damage2\_4. Depending on the photon energy, the absorption of an x-ray photon results in core-excited or core-ionized states. The relaxation of these highly excited states involves ultrafast intraatomic processes on the fs-timescale, such as radiative and Auger decays, which are highly sensitive to the initially populated states 5\_12. For the case that the excited or ionized species is embedded in an environment, interatomic processes are also possible 4,13\_16.

In principle, X-ray absorption spectroscopy (XAS) is a powerful tool to study the nearest environment of created core hole since it probes core-excited states below threshold, which are highly sensitive to the surrounding. However, for molecules as well as liquid or solid surroundings these core-excited states overlap significantly in the XA spectra, inhibiting access to the available information. This shortcoming can be overcome by using the subsequent resonant Auger process, as this detection method allows separation of overlapping states. In a liquid jet, this method applied to shallow core holes (like O 1s of the water molecule) mainly provides information from sites close to the liquid-solid interface, due to the short mean free path of the low-kinetic-energy Auger electrons. With a recently commissioned setup using tender X-rays we are now able to excite from deeper core levels like Cl 1s or K 1s, resulting in much faster Auger electrons, and as a consequence, a significantly deeper look into the liquid.

In this study, we investigate the electronic decay processes following XA of aqueous KCl at the K-edges of both K+ and Cl-. In particular, we investigate core-excited states below threshold, which undergo resonant Auger decay within less than 1 fs 16. Although the K+ and Cl- ions are isoelectronic, they reveal different fingerprints in the 2-dimentional maps formed by resonant Auger spectra. Based on complementary calculations we explain these findings with differences in the electronic structures of the two ions, thus conforming that the combination of XAS and AES techniques is a sensitive probe of the electronic structure of solutions.

Point 2:

The kinetic energy reported here for the Auger lines are ≅1 eV higher than the values reported in Ref 16. This can be explained with post-collision interaction (PCI) 17,18, which also cause in the normal Auger spectra of Fig. 2 and 3 for asymmetric lineshapes with a tail towards higher energies as can be seen clearly for the main peaks. More details are given in the SI.

Point 3

Instead, such states can be identified by using the resonant KL2,3L2,3 Auger decay which is schematically presented in the left part of Fig. 1. This is possible since the resonant Auger features differ significantly for the normal Auger features. In particular, the resonant Auger features of Cl- and K+ are quite different as can be seen in Figs. 2 and 3. In the 2D map of Cl- shown in Fig. 3 there are two dispersive resonant Auger features indicted with diagonal dashed lines, which both exhibit their maximum on the photon-energy axis at hν = 2825.2 eV indicating the excitation energy of a core-excited state. Its energy position is in good agreement with the value of the Cl- 1s-14p excitation … (as far as I understand the reference 19 and 20 it is for a Cl- as part of a molecule, if so, we should say this clearly.) On the kinetic-energy axis the maxima of these two diagonal dashed lines can be found at Ekin = 2374.6 eV and 2383.4 eV, indicating that they are related to the 1S and 1D main lines, respectively. For K+, no dispersive line related to the 1S main line can be identified due to the presence of a strong background.

Point 4

The resonant Auger spectra of both ions are similar in a way that they show dispersive lines caused by the spectator Auger decays of the 1s-14p excitations; these lines have their intensity maximum close to the normal Auger features. However, there is also a clear difference, which is caused by a non-negligible excitation of the dipole-forbidden 1s-13d state of K+ in solution. The spectator Auger decay of the latter state is well separated from all other Auger features, giving rise to the difference between K+ and Cl-.