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**Electron dynamics and intermolecular energy transfer in aqueous solutions studied by X-ray electron spectroscopy**[1]

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X-ray photoelectron spectroscopy measurements from a vacuum liquid microjet are performed to investigate the electronic structure of aqueous solutions. Here, focus is on the excited-state dynamics of chloride and hydroxide anions in water, following core-level excitation. A series of $Cl^-$(aq) charge-transfer-to-solvent (CTTS) states, and their ultrafast relaxation, on the time scale of the core hole, is identified from the occurrence of spectator Auger decay. Resonant oxygen 1s excitation of aqueous hydroxide, in contrast, leads to non-local decay, involving energy transfer into a neighboring water molecule. This channel is argued to arise from the weak hydrogen donor bond of $OH^-$(aq), and thus identifies a special transient hydration configuration, which can explain hydroxide's unusual and fast transport in water. Analogous measurements from pure water point to a similar relaxation channel, which is concluded from a strong isotope effect. The characteristic resonance spectral features are considerably stronger for $H_2O$(aq) than for $D_2O$(aq). As for $OH^-$(aq) the results can be understood in terms of energy transfer from the excited water molecule to a neighbor water molecule.

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