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**Comment on "Charge transfer to solvent dynamics in iodide aqueous solution studied at ionization threshold" by A. Kothe, M. Wilke, A. Moguilevski, N. Engel, B. Winter, I. Y. Kiyon and E. F. Aziz., Phys. Chem. Chem. Phys., 2015, 17, 1918**

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In ref.<sup>1</sup>, Kothe et al. investigate the photodynamics of an aqueous NaI solution, excited at 266 nm (4.66 eV) and photoionized at 350 nm (3.55 eV). They claim to populate charge-transfer-to-solvent (CTTS) states via electronic excitation above the ionization level in a two-photon process, which relax into different lower lying CTTS states. These CTTS states are then probed by photoionization. It is important to note, that these states are not the two different spin orbit components of the lowest CTTS state. Kothe's work raises a number of issues that are not addressed by the authors:

*The excited species.* Kothe et al. assume excitation of iodide by two-photon absorption. But at these photon energies also water molecules can be excited. In Kothe's work, the concentration of water molecules is about 2000 times larger than the iodide concentration. To unambiguously show that iodide is excited, a concentration-dependent measurement is inevitable. Indeed, assuming that water is excited instead of iodide can likewise explain the data without assumption of speculative states and decay routes: By absorption of two photons with 4.65 eV energy, an electron can be promoted from the water valence band into the conduction band<sup>2</sup>. The absorption of a probe photon with 3.55 eV then creates photoelectrons of  $2 \cdot 4.65 \text{ eV} + 3.55 \text{ eV} - 11.31 \text{ eV} = 1.54 \text{ eV}$ , which fits well to the observed weaker bound feature at 1.48 eV, i. e. the longer-lived signal may stem from an electron in the conduction band. We

may speculate that the feature at lower kinetic energies originates from cross-correlation signal (expected at 0.44 eV - see below) that is partly cut at low kinetic energies due to low transmission of the spectrometer or due to charged clusters around the liquid jet<sup>3</sup>. This would of course mean, that the pulse durations are longer than assumed in ref.<sup>1</sup> and that the temporal overlap is shifted. The authors did not provide information on how the temporal overlap was determined and we suppose that it was derived from the fitting procedure. The different rise times of the integrated electron signal of the two features (Fig. 4 of ref.<sup>1</sup>) would also support this assignment.

*The role of multi-photon processes.* The authors do not show any intensity-dependent measurements supporting the assignment of a two-photon excitation. The pump pulse intensity is two orders of magnitude lower than the probe pulse intensity, which questions this assignment.

*The decay of the CTTS states and its decay product.* The authors of ref.<sup>1</sup> interpret their data on the basis of a previous resonant Auger spectroscopic study on aqueous chloride solution<sup>4</sup>, in which the CTTS states are populated by the transition  $2p \rightarrow \text{CTTS}$ . This situation cannot be compared to the present iodide case: First, the solvation shell of chloride is much smaller than of iodide. Second, the two holes created in the Auger process may significantly stabilize the chloride CTTS states.

In the UV spectra of iodide, a number of different CTTS bands are observed. The lowest CTTS bands in water appear at 5.48 eV, 6.34 eV and 6.7 eV (so-called B<sub>1</sub> band)<sup>5</sup>. If the weaker bound state observed by Kothe et al. was the B<sub>1</sub> state, a binding energy of 1.33 eV is expected, which is much lower than the observed one. For the same argument, even higher CTTS states can be excluded.

Regardless of the energetics, CTTS states are known to decay forming a solvated electron which have been observed also in the previous photoelectron studies. Its vertical binding energy is

$\sim 3.4\text{ eV}^{6,7}$ , the distribution of binding energies however is broad ( $\sim 1\text{ eV}$ ). With probe photon energies of  $3.55\text{ eV}$ , signal from the hydrated electron should be observable. The hydrated electron in water is very long-lived and gives rise to signal beyond ns. In addition, if the very diffuse CTTS state can be observed, also the hydrated electron should be observable in terms of photodetachment cross-sections. Kothe et al. do not provide any reason why the hydrated electron should not be produced in their experiment.

*The assignment of the one-color spectra* differs from that of earlier work<sup>6</sup> in the sense that hydrated electrons are not required to reconstruct the spectra, but the  $3a_1$  band of water is used in addition. For the reconstruction, Kothe et al. considered the binding energies as determined from static photoemission but they ignored the expected intensity ratios. The intensity ratios of the two water bands,  $I_{3a_1} : I_{1b_1}$ , are  $1 : 4$  ( $266\text{ nm}$ ) and  $25 : 1$  ( $355\text{ nm}$ ), while the expected ratio is  $\approx 1 : 2$  (ref.<sup>8</sup>). For the iodide bands, intensity ratios  $I_{I_{3/2}} : I_{I_{1/2}}$  of  $30 : 1$  ( $266\text{ nm}$ ) and  $1 : 10$  ( $355\text{ nm}$ ) are used in ref.<sup>1</sup>, while from dipole selection rules a ratio of 2:1 is expected. Three possible arguments may be used to explain these discrepancies. First, different detuning from intermediate resonances in the multi-photon processes influences the intensity ratio, but such a huge change is very unlikely. Second, non-linear effects do play a role in multi-photon processes; however, signal ratios are taken for features generated by the same number of absorbed photons, i. e. the intensity dependence will cancel out. Third, there might be some minor effects from kinetic-energy dependent cross-sections, but the kinetic energies of the corresponding peaks are actually quite similar and cannot explain these huge changes in intensity ratios, either.

*The cross-correlation signal in the pump-probe data is missing.* Cross-correlation signal due to photodetachment of iodide (two- and three-photon process) and photoionization of water (three-photon process) below  $3\text{ eV}$  is expected at

$0.17\text{ eV}$  (absorption of one pump and one probe photon, '1+1'), at  $0.44\text{ eV}$  and  $2.79\text{ eV}$  (1+2), and at  $1.54\text{ eV}$  (2+1), but missing. Ionization channels that contribute to the  $3.55\text{ eV}$  one-color signal should also contribute to the cross-correlation signal. There is no reason why a replacement of one  $3.55\text{ eV}$  photon by one  $4.65\text{ eV}$  photon should not result in observable signal at temporal overlap. In principle, the same argument also applies for the  $4.66\text{ eV}$  one-color signal, provided that the totally absorbed photon energy still exceeds the ionization energy. In combination with the assignment of the one-color spectra, this shows that Kothe's interpretation of the data is not self-consistent.

*The correspondence between Kothe's data and fluorescence up-conversion data<sup>9</sup>* in terms of binding energy and emission energy is accidental. Kothe et al. measured the energy difference between excited state and ionic state, while Messina et al. measured the energy gap between excited state and ground state. These two values are not related.

*The meaning of the intermediate I state*  
The scattering between the few individual data points in Fig. 4 of ref.<sup>1</sup> is significantly larger than the difference between the two models. Therefore, the need of the intermediate I state is not evident. Unfortunately, in ref.<sup>1</sup> no support for this state from literature could be provided which makes this intermediate state purely hypothetical. To get a better feeling for the results provided in ref.<sup>1</sup>, it would be very helpful to know the errors of the retrieved lifetimes.

Although the experiment is certainly very interesting, the interpretation of the data seems to be rather arbitrary and lacks support from literature. Some very important tests to prove the interpretation are missing (intensity and concentration dependence). It would also be very interesting to vary the pump photon energy to investigate the nature of the suggested X state.

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