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Reply to the 'Comment on "Charge Transfer to Solvent Dynamics in Iodide Aqueous Solution Studied at Ionization Threshold"' by A. Lübcke and H.-H. Ritze, Physical Chemistry Chemical Physics, 2015, 17, C5CP00346F

Alexander Kothe^a, Martin Wilke^a, Alexandre Moguelevski^a, Nicholas Engel^a, Bernd Winter^a, Igor Yu. Kiyan^{*a} and Emad F. Aziz^{‡a,b}

The role of experimental conditions in the study of the early-time charge transfer to solvent dynamics in iodide aqueous solution is revised. Under the short (~ 50 fs) laser pulse regime of the current experiment, the presence of the pump-probe cross-correlation signal in the transient photoelectron spectra can be ruled out due to the much larger time scale of the electron-transfer dynamics. The ratio of the ionization yields from different initial states of iodide and water is argued to be dependent on the electron kinetic energy, and to be influenced by the presence of a bound resonance state above the vacuum threshold. Re-evaluation of our experimental data reassures the presence of an intermediate state in the charge-transfer process, initiated by electronic excitation into the continuum spectrum.

In their Comment¹, Ritze and Lübcke raise two new issues which we would like to address. The first concerns the spectral contributions to one-color spectra, and the second point regards the presence of cross-correlation signal in the transient spectra. All other issues raised in the Comment are already discussed in our initial work², and only a few clarifying comments will be provided at the end.

Contributions to one-color spectra. Based on ionization spectra from liquid water obtained with the use of synchrotron radiation³, and considering the statistical weights of the spin-orbit states of iodine, Ritze and Lübcke claim that signal intensity ratios of the $^2P_{3/2}$ and $^2P_{1/2}$ iodide bands and the $3a_1$ and $1b_1$ water bands reported in Ref.² are unreasonable.

According to Fermi's golden rule, the ionization probability has the form

$$w \propto |A_{if}^N|^2 \rho(E_f) \quad (1)$$

where A_{if}^N denotes the N -photon matrix element of the transition from the initial ground state $|i\rangle$ to the continuum state $|f\rangle$ and $\rho(E_f)$ is the density of continuum states at the final kinetic energy E_f of the photoelectron. If the interaction between the ejected electron and the residual core is neglected, the density of continuum states is proportional to $\sqrt{E_f}$. One

can immediately see that in the limit of small kinetic energies, representing the case of Ref.², a finite increment in E_f can lead to a change in $\rho(E_f)$ by a large factor. Thus, the yield ratio of ionization channels can vary significantly in the vicinity of the ionization threshold. Furthermore, the dependency of the ionization yield on the kinetic energy can be affected by the presence of a bound state within the continuum. In this case the kinetic energy spectrum acquires a shape of Fano profile⁴. As discussed in our work², charge-transfer-to-solvent (CTTS) states lying above the vacuum threshold play an important role in the population dynamics of the lower CTTS states. The observed signal ratios in the one-color spectra can be thus attributed to the existence of a resonant bound state lying at ~ 1.5 eV above the threshold, with the Fano parameter $q \gg 1$.

It should also be noted that even a change of photoionization energy from 60 eV^3 to 38.4 eV^5 yields an almost twice as large contribution ratio of the $3a_1$ and $1b_1$ water bands. Furthermore, one needs to keep in mind that signal ratios strongly depend on the anisotropy parameters, i.e., on the angle at which the photoelectrons are detected with respect to the light polarization vector.

Cross-correlation signal. Ritze and Lübcke argue that the cross-correlation signal needs to be considered for the interpretation of the data. They also speculate that this signal might dominate in the transient spectra if the pulse duration of the pump and probe beams is much larger than the specified value of 60 fs. This can be ruled out though since the beam diagnostic tools were applied in the experiment to measure pulse durations and beam-optics dispersion in the paths of the pump and probe beams was carefully taken into account. A typical laser

^a Joint Laboratory for Ultrafast Dynamics in Solutions and at Interfaces (JULiq), Institute of Methods for Material Development, Helmholtz-Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany.

Fax: 49 30 8062 14757; Tel: 49 30 8062 12927

^b Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

* E-mail: igor.kiyan@helmholtz-berlin.de

‡ E-mail: emad.aziz@helmholtz-berlin.de

pulse duration of 55 fs in the UV/visible range was also measured in our recent experiment where we employed the cross-correlation technique with the use of XUV light from high-order harmonic generation⁶. We do not completely exclude cross-correlation signal contributions to the transient spectra but this would affect only time delays very close to zero, and will not change our interpretation.

In the following, a few other points will be clarified shortly.

(1) Two-photon excitation of water giving rise to the observed electron signal would be in disagreement with Ref.⁷ where no evidence for electronically excited transient states in water was found for 2-photon excitation/1-photon ionization at experimental conditions comparable to the conditions applied in Ref.². This was already mentioned in Ref.².

(2) It is not clear to us why the $2p \rightarrow$ CTTS excitation in chloride aqueous solution should not be analogous to $I_{(aq)}^-$. How the size of the hydration shell may affect the population of CTTS state is not known, and we have no reason to rule out the existence of CTTS-type states above vacuum threshold. Furthermore, the final state in the core-level excitation study of chloride aqueous solution⁸ is a 1-hole and not a 2-hole state unlike stated in the Comment¹.

(3) The binding energy of the solvated electron in aqueous solution is known to have a value between 3.3 and 3.6 eV^{9,10}. In a photoelectron study, it is highly improbable that this species is observable with probe photons of 3.55 eV.

(4) It is true that in our experiment² an ionized state is created while in the fluorescence study¹¹ the charge state of the solute is not changed. However, we expect that this has a fairly small effect on the energies of the relevant electronic states, consistent with Ref.¹². Note also that it is common to combine photoelectron and optical absorption data for determination of the absolute energy levels in aqueous solution¹³. Hence we strongly disagree with Ritze and Lübcke that the matching energies presented in Figure 3c of Ref.² are accidental. We do admit though (and this is already mentioned in Ref.²) that at the present moment we have no satisfactory suggestion as to how to simultaneously interpret the two studies. Additional experiments are needed.

(5) As explained in detail in Ref.², the temporal evolution of the ionization yield from the transient states can be better described when assuming an intermediate state *I*. In order to support further this statement, we have calculated the adjusted coefficient of determination, \bar{R}^2 , which represents a comparative measure of model suitability. The adjusted R^2 values of 0.91 and 0.88 were obtained for the models with and without taking the intermediate state into account, respectively. The fact that such a state has not been previously observed for iodide is barely an argument against our interpretation.

(6) The interpretation of our results² relies on a careful analysis of the electronic structure of the NaI aqueous solution, partially aided by assignments found in the literature.

The measurements of the intensity and concentration dependencies of the transient signal would make the study more comprehensive, but they are not required for the conclusions drawn here. One should also note that such additional studies are not straightforward, and require consideration of other effects. For example, the variation of the NaI concentration leads to a change in the streaming potential that influences the peak positions in the photoelectron spectra¹⁴. In the intensity study, saturation of the two-photon transition¹⁵ and the presence of resonant states (as mentioned in Ref.²) can result in a polynomial dependency of the transient signal with an exponential coefficient smaller than 2.

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