Can Current Experimental Data Exclude Non-Gaussian Genuine Band Shapes in Ultraviolet Photoelectron Spectra of the Hydrated Electron?

ABSTRACT: Two recent articles present results that allegedly exclude a possible multimodal distribution of the hydrated electron in ultraviolet photoelectron spectra. The first article bases its conclusion on the assumption that the non-Gaussian genuine band shape previously retrieved for the solvated electron in liquid water is an artifact arising from insufficient electron scattering cross sections used in the retrieval. The second article excludes a multimodal band shape based on a photoelectron spectrum of the solvated electron in water clusters recorded at a single ultraviolet photon energy, and it further assumes that cluster results are transferable to the liquid without further justification. Here, we show that based on current data multimodal distributions cannot be unambiguously excluded. Furthermore, the transferability of cluster results to the liquid can be neither justified nor refuted on the basis of currently available experimental ultraviolet photoelectron spectra.

A recent article by David Bartels addresses the issue of the band shape of the genuine electron binding energy (eBE) spectrum of the solvated electron in liquid water. The article states that the genuine eBE of the hydrated electron must be single Gaussian in shape, contrary to the non-Gaussian shape derived in ref 2 from a simultaneous fit of scattering simulations to 11 experimental liquid photoelectron spectra recorded at 11 different ultraviolet (UV) photon energies below 5.8 eV. Reference 1 concludes that the non-Gaussian ("bimodal") distribution found for the genuine eBE in ref 2 must have resulted from deficiencies in the scattering cross sections used in the simulations, arising from an allegedly wrong value of \( V_0 = -1.0 \) eV for the escape barrier. Reference 1 suggests that the scattering cross sections be refitted with a more realistic choice of \( V_0 \), i.e. with \( V_0 \) closer to \( \sim -0.1 \) eV, and predicts that the refitted cross sections would result in a genuine eBE spectrum with Gaussian shape.

We have performed the suggested refitting and found that no satisfactory agreement with the set of experimental spectra from ref 3 could be achieved for \( V_0 = -0.1 \) eV and a Gaussian genuine distribution. More detailed explanations are provided in ref 4. Figure 1 illustrates this for the example of the photoelectron spectrum recorded at 5.8 eV photon energy. The black line shows the experimental photoelectron spectrum together with a scattering simulation (green line) for an escape barrier of \( V_0 = -1.0 \) eV, the original electron scattering cross sections determined in refs 2, 5, and 6, and the non-Gaussian genuine band shape derived in ref 2. The agreement between experiment and simulation is almost perfect. The red line shows the simulated photoelectron spectrum obtained with cross sections refitted for a barrier \( V_0 = -0.1 \) eV and a single Gaussian genuine spectra as suggested in ref 1. It is obvious that the simulation with a single Gaussian genuine spectrum and refitted cross sections for a lower escape barrier does not reproduce the experimental shape.
From what we currently know, we can thus exclude energies (see also Figures 3 and S9 in ref 2). In other words, edge of the experimental spectra recorded at higher photon multimodal distribution is needed to reproduce the high eBE genuine band shape. This clearly demonstrates that a experimental spectra, contrary to the statements in ref 1. The multimodal structure is clearly contained in the experimental spectra, contrary to the statements in ref 1. From what we currently know, we can thus exclude deficiencies in the used scattering cross sections as a source for an artificial multimodal distribution. However, as already pointed out in ref 4, we cannot completely exclude other potential artifacts. Among them could be unknown biases in the experimental UV spectra used in ref 2 that might pretend a distorted genuine distribution. Currently, there is not enough evidence to decide beyond any reasonable doubt whether the multimodal genuine distribution in the UV photoelectron spectra of liquid water is a true distribution or caused by artifacts. We note, however, that the linear response properties of liquid water do not exclude multimodal genuine band shapes, contrary to what ref 1 wants to suggest. Obviously, the same is true for the reverse: If experiments were eventually to confirm the multimodal band shape, this would not conflict with a linear response behavior of the liquid.4

Our previous work in ref 7 had already shown that the photoelectron spectrum of the hydrated electron in large water clusters (with ~300 molecules per cluster) recorded at a single photon energy of 4.66 eV is consistent with a single Gaussian genuine band shape. In the same work, we have also shown that this 4.66 eV photoelectron spectrum does not allow us to exclude a multimodal (“bimodal”) genuine band shape, i.e., a non-Gaussian band shape.7,8 This is again visualized in Figure 2, which displays the binned experimental spectrum with error bars (cyan shaded area) together with the cluster simulations for a single Gaussian genuine distribution (black full line) and a multimodal genuine distribution (black dashed line). Both simulations agree equally well with the experiment. At 4.66 eV, photons simply do not have enough energy to cover the non-Gaussian part of the genuine eBE spectrum derived in ref 2. These photons thus essentially probe only the dominant Gaussian component of the genuine spectrum (see for clusters Figure 2 and Figure 2 in ref 7, and for the liquid Figures 3, S5, and S9 in ref 2). This is in contrast to the photoelectron spectrum recorded at 5.8 eV, which probes the entire multimodal genuine spectrum (Figure 1). Figure 2 also compares our cluster spectrum with corresponding liquid jet spectra from refs 2 and 3 recorded at a photon energy around 4.6 eV. The cluster spectrum coincides with the 4.6 eV liquid spectrum within the error, while the 4.8 eV liquid spectrum seems to deviate slightly from the cluster experiment on the high eBE edge. It would be rash to take such similarities as evidence for the transferability of cluster results to the liquid. In general, differences between clusters and liquid are not implausible, e.g. if one considers that cluster temperatures in supersonic expansions are lower than those in liquid microjets. Differences might be hidden in the high eBE part of the distribution cut off at photon energies around 4.6 eV. In a recent article, Svoboda et al. claim that they can exclude a multimodal (“bimodal”) distribution for the hydrated electron based on a photoelectron spectrum recorded for the solvated electron in water clusters at a single photon energy of 4.66 eV (see Figure 3), i.e. the same energy as used in our previous cluster work (Figure 2, ref 7). The authors cite an improved signal-to-noise ratio of their cluster spectra to support their claim but do not offer any model predictions of the expected differences between the observable band shapes resulting from single Gaussian and multimodal genuine band shapes. Figure 2 illustrates that for cluster spectra recorded at 4.66 eV the expected difference between a single Gaussian genuine band shape (full line) and the multimodal genuine Gaussian band shape (dashed line) is in fact small and limited to electron kinetic energies (eKE) below about 0.5 eV. Quantitative measurements in this low-eKE range are particularly prone to experimental uncertainties. Given the small difference between single Gaussian and multimodal band shapes in a 4.66 eV spectrum (Figure 2), the authors’ statement in ref 9 that their spectra (Figure 3) “exclude a possible bimodal distribution” appears rather audacious. They also quote liquid results to support their conclusion (see

Figure 2. eBE spectra of the hydrated electron at photon energies around 4.6 eV. Cyan trace: Experimental cluster spectrum from ref 7. The raw data (see Figure 2a in ref 7) were binned with resolution of 0.1 eV. The width of the trace indicates three standard deviations from the mean. Red and green trace: experimental liquid spectra from ref 3 for hν = 4.6 and 4.8 eV, respectively. Black traces: simulated cluster spectra assuming a single (1G) Gaussian genuine band shape (full line) and the multimodal (3G) band shape from ref 2 (dashed line) as in ref 7.

Figure 3. Experimental eBE spectra of the hydrated electron recorded at photon energies around 4.6 eV. Blue trace with fit: Cluster spectrum adapted from ref 9. The spectrum was copied from Figure S4d of ref 9 and adapted under Creative Commons Attribution NonCommercial License 4.0. The liquid spectra are scaled to match the leading (low eBE) edge of the Gaussian fit of ref 9 (black trace). Red and green trace: liquid spectra from ref 3 for hν = 4.6 and 4.8 eV, respectively.
below). However, compared with clusters, the expected difference between a single Gaussian and a multimodal genuine band shape is even less pronounced in the liquid as shown in Figure 4.

Figure 4. Upper spectra: Genuine eBE spectrum for the hydrated electron in liquid water with 3 Gaussians as derived in ref 2 (black full line) and 1 Gaussian (blue dashed line). The gray shaded area indicates the fit error determined in ref 2 for the genuine spectrum. Lower spectra: Simulation of observed liquid jet eBE spectra at a photon energy of 4.6 eV for the genuine distribution with 3 Gaussians (black full line) and for the genuine distribution with 1 Gaussians (blue dashed line) shown in the upper trace. The simulations employ the original cross sections’ and an escape barrier of $V_0 = -1.0$ eV. The gray shaded area indicates the uncertainty due to the fit error in the genuine spectrum. The simulated spectra for the two different genuine spectra are almost identical. The figure clearly reveals that spectra observed at 4.6 eV cut off the non-Gaussian part of the genuine spectra. This also holds for lower photon energies.2

The authors of ref 9 also quote the article by Bartels1 in support of their claim. As mentioned above, the latter, however, refers to liquid water, not water clusters. It is thus instructive to compare the cluster spectrum of ref 9 directly with the corresponding liquid jet spectra from refs 2 and 3 recorded at photon energies around 4.6 eV. The comparison in Figure 3 shows a marked difference between cluster and liquid in the high eBE (low eKE) range. Even if the exclusion of a possible multimodal distribution of the hydrated electron as stated in ref 9 were justified for clusters, such a statement would appear not to be simply transferable to the liquid, given the difference between the cluster and the liquid spectrum in Figure 3. Instead, the conclusion would have to be that the measurements of ref 9 suggest a significant difference between hydrated electrons in clusters and in the liquid. Therefore, the authors of ref 9 cannot rely on arguments for the liquid in ref 1 to support their claim regarding the exclusion of multimodal distributions. On top of that, the arguments put forward in ref 1 against the multimodal genuine band shape derived in ref 2 for the liquid have actually proven to be incorrect as discussed here in the context of Figures 1 and 4, and in ref 4.

In this context, we note that the justification provided in ref 1 for a value of the escape barrier around $V_0 = -1.0$ eV is based on the lower bound derived in ref 12. The derivation of that lower bound actually contained a sign error, as already pointed out in ref 11 and subsequently in refs 4 and 10. In fact, the cluster data by Coe et al. in ref 12 provide only a lower bound of $V_0 \geq -1.72$ eV; that means, they favor neither $-1.0$ eV nor $-1.0$ eV. Moreover, it remains unclear whether these cluster data are at all representative for the liquid. A definite value of $V_0$ is still not available for liquid water. We have recently suggested a new droplet experiment that is sensitive to the properties of the escape barrier.13 This work also highlights that the determination of $V_0$ is more complicated than might appear at first sight. What is important for the current work is that our simulations of the UV spectra of the hydrated electron are largely insensitive to the exact value of $V_0$ as demonstrated in Figure 1 (see also Figure 1 in ref 4).

We do not believe that currently available data for clusters7,9 recorded at a single photon energy of 4.66 eV are sufficient to determine the genuine band shape of the solvated electron in clusters unambiguously—not even to decide whether it is single Gaussian or multimodal. More importantly, the measurements on clusters in ref 9 do not allow one to judge the band shape in the liquid (Figures 2–4). Generally, the determination of the genuine band shape requires systematic measurements with photon energies covering the whole range well beyond the high eBE edge of the genuine band. While such data is not yet available for clusters, corresponding measurements have already been performed for the liquid up to photon energies of 5.8 eV.3 The resulting liquid jet spectra clearly suggest a non-Gaussian genuine band shape.2 Contrary to the speculation in ref 1, this is by no means indicative of deficiencies in scattering cross sections used in the analysis (Figure 1, ref 4). Instead, the deviation from a single Gaussian genuine band shape is directly evident in the experimental spectra of the liquid. Currently available data neither allow one to unequivocally decide whether the genuine distribution of the hydrated electron in the UV is single Gaussian or multimodal nor do they provide conclusive evidence for the transferability of cluster results to the liquid. For a final resolution of these issues based on experimental data there is no way around further extensive measurements of both clusters and the liquid.

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Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

I thank all current and former members of my research team who have contributed to the previous experimental and theoretical work which is discussed in the current publication. I am grateful to Prof. Toshinori Suzuki and his group for making their liquid jet spectra available. This project has received funding from the European Union’s Horizon 2020 research and innovation program from the European Research Council under the Grant Agreement No. 786636, and the research was supported by the NCCR MUST, funded by the Swiss National Science Foundation (SNSF), through ETH-FAST, and through SNSF Project No. 200020_172472.

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