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Dear Editors,

Please find enclosed our manuscript entitled

"The all-seeing eye of resonant Auger electron spectroscopy: a study on aqueous solution using tender x-rays"

by

Dr. Tsveta Miteva, Dr. Nikolai V. Kryzhevoi, Dr. Nicolas Sisourat,

Dr. Christophe Nicolas, Dr. Wandared Pokapanich, Dr. Thanit Saisopa,

Dr. Yuttakarn Rattanachai, Prof. Dr. Andreas Dreuw, Dr. Jan Wenzel,

Dr. Jérôme Palaudoux, Dr. Gunnar Öhrwall, Dr. Ralph Püttner,

Prof. Dr. Lorenz S. Cederbaum, Dr. Jean-Pascal Rueff, and Dr. Denis Céolin

to be considered for publication in the Journal of Physical Chemistry Letters in the subject category "Spectroscopy and Photochemistry; General Theory".

X-ray absorption and resonant Auger spectroscopies are well-established tools to study the electronic structure and light-induced processes of liquids. In this manuscript for the first time we employed a combination of these two spectroscopies in the tender x-ray regime, which was only possible thanks to the state-of-the-art liquid microjet technique combined with the last generation of synchrotron radiation facilities. These experimental techniques allowed us to study specifically the bulk of the solution, and moreover, to explore hitherto unaddressed electronic transitions. On the example of aqueous KCl, we observed that the K-shell Auger spectra of the isoelectronic K^+ and Cl^- ions recorded for a range of photon energies exhibit remarkably different features. With the aid of high-level *ab initio* calculations, we explain these differences as resulting from the modified electronic structure in the presence of the solvent molecules, which leads to the population of dipole-forbidden states.

Near-edge X-ray absorption spectroscopy (NEXAFS) is more sensitive to the surrounding than other core-level spectroscopies, such as photoelectron spectroscopy, since it allows one to directly probe unoccupied electronic states. Moreover, in combination with resonant Auger spectroscopy one can obtain additional detailed information. Unlike soft x-rays which predominantly probe the surface of the target liquid, with tender x-rays one can explore the bulk of the liquid due to the high energy of the outgoing Auger electrons and thus reduce specific effects related to the interface. This can have important implications in the study of solvated ions, for example, Fe, Cu, Mn, Zn, Co, Ni, Ca, etc. which have deep core levels and play an essential role in the proper functioning of living organisms. The results reported in our manuscript aim at paving the way to the fundamental understanding of the processes initiated by x-ray absorption in biologically relevant systems.

We therefore think that the present article may interest a broad range of scientists and also incite further investigation on the topic.

Please find below the names and the contact information of 3 suggested reviewers, who have profound knowledge of resonant Auger and x-ray absorption spectroscopies in liquids due to their own research projects:

Prof. Dr. Richard Saykally (*soft x-ray absorption spectroscopy of liquids*)
UC Berkeley: College of Chemistry
saykally@berkeley.edu

Dr. Bernd Winter (*properties and light-induced phenomena of liquids using liquid jet photoelectron spectroscopy*)
Fritz-Haber-Institut der Max-Planck-Gesellschaft
winter@fhi-berlin.mpg.de

Prof. Dr. Olle Björneholm (*synchrotron radiation-based spectroscopic techniques for liquids and clusters/nanoparticles*)
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olle.bjorneholm@physics.uu.se

With the submission of this manuscript we would like to undertake that none of the material reported in the above mentioned manuscript has been published or is under consideration elsewhere. Preceding this submission, the manuscript was sent to the Journal of American Chemical Society (manuscript ID ja-2018-021822, editor: Peter J. Stang).

Sincerely,

Dr. Denis Céolin