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Liquid-jet photoemission spectroscopy as a structural tool: site-specific acid–base chemistry of vitamin C†

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Liquid-jet photoemission spectroscopy (LJ-PES) directly probes the electronic structure of solutes and solvents. It also emerges as a novel tool to explore chemical structure in aqueous solutions, yet the scope of the approach has to be examined. Here, we present a pH-dependent liquid-jet photoelectron spectroscopic investigation of ascorbic acid (vitamin C). We combine core-level photoelectron spectroscopy and *ab initio* calculations, allowing us to site-specifically explore the acid–base chemistry of the biomolecule. For the first time, we demonstrate the capability of the method to simultaneously assign two deprotonation sites within the molecule. We show that a large change in chemical shift appears even for atoms distant several bonds from the chemically modified group. Furthermore, we present a highly efficient and accurate computational protocol based on a single structure using the maximum-overlap method for modeling core-level photoelectron spectra in aqueous environments. This work poses a broader question: to what extent can LJ-PES complement established structural techniques such as nuclear magnetic resonance? Answering this question is highly relevant in view of the large number of incorrect molecular structures published.

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1 Introduction

Photoemission (PE) spectroscopy from the liquid phase was made possible *via* the liquid-microjet (LJ) technique,¹ and has since become an increasingly applied tool for studying aqueous solutions as it directly probes the liquid

channel in the present work. One of the limiting factors for a wider-community application of LJ-PES as a chemical analysis tool can be the need for suitable X-ray sources, usually limited to synchrotron-based facilities. However, recent developments of laboratory-based sources relying on high-harmonic generation (HHG) promise to significantly ease access to table-top X-ray generation, possibly vastly increasing the number of studies in the near future.^{17–20}

Utilizing chemical shifts revealed by photoelectrons from solution to gain structural insight appears to provide a promising complementary route to powerful structural analysis techniques such as nuclear magnetic resonance (NMR).²¹ It took many years for NMR to be fully developed and established as a conventional structural tool. Yet, even the well-established NMR has witnessed surprisingly frequent structural misassignments. This is especially the case for natural products, an important group of compounds in drug development. There are hundreds of reportedly misassigned structures of even medium-sized molecules.^{22–25} The present work should contribute to the development of LJ-PES as a complementary tool for chemical (structural) analysis for molecules solvated in liquids. It could extend the portfolio of techniques to analyze the structure of liquids from the perspective of individual atoms, *i.e.*, useful to decipher molecular structure and speciation.

LJ-PES has been successfully applied, *e.g.*, to study interactions of hydroxide ions (OH^-) with water,²⁶ different charge states of amino acids,²⁷ or specific solvation structures of biomolecules.^{28,29} The technique could even trace minor conformational changes following solvation.³⁰ Recently, we have demonstrated that when combined with theoretical modeling, LJ-PES is able to reveal acid–base transformations in complex cases.³¹ For example, in the case of the glucose molecule, we have shown that the specific deprotonation site out of five candidates in the molecule can be unequivocally assigned using C 1s core-ionization spectra when comparing with calculated spectra modeled for each hypothetical deprotonation center. Core-electron BEs contain site-specific information on the chemical environment, reflecting the molecular structure of the ionized site. We identified the real deprotonation center based on spectral shape and peak positions, *i.e.*, only one of the modeled spectra matched the measured one. This proved the ability of the combined theoretical-experimental approach to site-specifically probe the acid–base chemistry of a molecule in an aqueous solution. The immediate follow-up question is how general such an approach is and whether the technique is also applicable in the case of multiple subsequent deprotonation events.

With that in mind, the current study focuses on the acid–base equilibria of vitamin C (*L*-ascorbic acid) revealed from LJ-PES. This vital water-soluble micronutrient has attracted much attention since the first pioneering studies of Albert Szent-Györgyi in the 1920s.³



Fig. 2 Molecular structures of vitamin C in its fully protonated, singly deprotonated, and doubly deprotonated form. Two fully protonated tautomers, four hypothetical single deprotonation sites, and six hypothetical double deprotonation sites of the A tautomer are shown.

molecular structures. Therefore, the methodological aspects of the computations are explored. We present an efficient computational approach to model the spectra from a single molecular geometry based on the maximum-overlap method and compare the protocol to calculations from an ensemble of structures.

2 Methods

2.1 Experiments

LJ-PES measurements were performed at the P04 soft-X-ray beamline at PETRA III⁴⁰ (DESY, Hamburg, Germany) using the EASI setup.⁴¹ A vacuum LJ of $\sim 26 \mu\text{m}$ diameter was ejected with a velocity of $\sim 25 \text{ m s}^{-1}$ via a fused-silica nozzle. A high-performance liquid chromatography (HPLC) pump was used for solution delivery with a constant flow rate of 0.8 ml min^{-1} . The temperature of the ascorbic-acid aqueous solution after injection was estimated to be in the range of 279–283 K in the laminar region of the LJ, which typically extends for 5–10 mm from the capillary into vacuum.^{1,2} This laminar region is brought into overlap with the X-ray beam and the photoelectron detection axis. The liquid subsequently freezes and is collected by a liquid-nitrogen-cooled trap at the far end of the interaction chamber. A small metallic tube, placed into the main polyether ether ketone (PEEK) liquid-delivery line, enables electric grounding of the liquid or application of a

core-electronic levels, *i.e.*, aiming at highly excited states of the ions. Here, the core-valence separation can be used in conjunction with EOM-CC,^{53,54} representing the state-of-the-art approach. Alternatively, the maximum-overlap method⁵⁵ (MOM) can be used. MOM is based on modifying the convergence criteria to not only minimize eigenvalues but also to maximize overlap with the orbitals from the previous step. In this way, the approach prevents the variational collapse of the wavefunction and keeps the hole in the desired orbital. This represents an efficient and accurate approach as MOM can be combined with any electronic-structure method and includes full electronic relaxation. Based on our previous experience,³¹ we aim to utilize MOM in this way to describe core-level ionization in this study.

The most efficient approach to cover the solvation effects is using the dielectric continuum model.⁵⁶ It is mandatory to use its non-equilibrium form to separate the fast electronic and slow nuclear response.^{57,58} The specific solvent effects can be conveniently added within cluster-continuum models^{59,60} by including a few closest solvent molecules into the quantum-mechanical calculation explicitly, while the rest is represented by the dielectric continuum. However, when dealing with systems exhibiting highly concentrated charges, *e.g.*, containing O^- groups, a large number of explicit solvent molecules may be required to achieve convergence.^{61,62} Alternatively, the QM/MM (quantum mechanics/molecular mechanics) or fragmentation techniques can be used.^{63,64}

2.3 Calculations

2.3.1 Photoelectron spectra from a single optimized structure. We modeled the PE spectra for two fully protonated tautomers and for all hypothetical singly and doubly deprotonated forms of the A tautomer of ascorbic acid to compare them to the experimental data. In total, we used two fully protonated (A and B tautomers), four singly deprotonated (on the hydroxyl groups of C2, C3, C5, and C6), and six doubly deprotonated forms, as shown in Fig. 2. The optimizations were performed using the hybrid functional based on the B3LYP functional with the Coulomb-attenuating method, together denoted as CAM-B3LYP,⁶⁵ and Pople's basis set 6-31+G*. This choice is based on our previous experience and testing.³¹ All optimized structures were confirmed to be real minima by the absence of imaginary vibrational frequencies. To mimic the solvent polarization effects, the polarizable continuum model^{66,67} (PCM) was used in the optimization. Default PCM parameters, *i.e.*, universal force field (UFF) atomic radii⁶⁸ and an electrostatic scaling factor $\alpha = 1.1$, were used. Furthermore, each singly deprotonated molecule contained six water molecules placed around the deprotonated hydroxyl group (O^-), and each doubly deprotonated molecule contained

D2 dispersion correction.⁸⁰ The MM part modeling the water molecules was described by the TIP3P model.⁸¹ The temperature was kept constant at 280 K (close to the experimental conditions) during the simulation using the Nosé-Hoover thermostat.^{82,83} With this approach, we ignore nuclear quantum effects; however, they are usually not of significance for modeling PE spectra in the liquid phase.⁸⁴ The initial droplet structure was created by the Packmol code,⁸⁵ and the QM/MM simulation was performed with our ABIN code⁸⁶ connected to Terachem, version 1.93.^{87,88} The total simulation length was 50 ps, with a time step of 0.5 fs. The first 10 ps were discarded as equilibrating period. From the remaining 40 ps, 100 geometries which contained the same number of explicit water molecules as in the single optimized geometry calculations were extracted, *i.e.*, 0, 6, and 12 water molecules for fully protonated, singly deprotonated, and doubly deprotonated forms, respectively. These water molecules were again chosen to be the closest to the deprotonated O^- sites. The sampled geometries can be found in the ESI†

The extracted 100 geometries for each protonated form were used as input for core-level binding-energy calculations employing exactly the same methodology as described for the single-geometry calculations. The resulting spectrum was again constructed from individual Gaussian functions with the same widths as detailed above.

3 Results and discussion

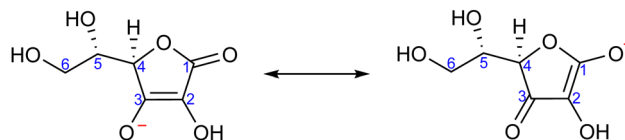
3.1 Core-level C 1s ionization for a site-specific probing of acid-base structure

Our goal is to demonstrate the potential of LJ-PES for elucidating structural information. For this, we focus on the well-described example molecule of vitamin C and show that the chemical insight obtained from LJ-PES can be as good as the one achieved from NMR studies, with LJ-PES having the additional capabilities described in the introduction.

Experimental and theoretical PE spectra for all three protonation states are presented in Fig. 3, panels A–C. Experimental spectra measured using a precise photon energy of 400.88 ± 0.02 eV are plotted in black and theoretical spectra are colored as indicated. We first focus on C 1s core-level PE spectra for pH = 2 (panel A) and pH = 7 (panel B), where the fully protonated and singly deprotonated forms of ascorbic acid are expected to be present.³⁹ The results for pH = 13 (panel C), extending our approach to double deprotonation for the first time, are discussed

(green dashed line). The modeled spectrum of the A tautomer agrees excellently with the experiment both in shape and position. From the theory, we can assign the smaller peak to ionization of the C1 site (see Fig. 1 and Table 1) while the main peak is from the combined signal of the other five carbon sites in the molecule. The main peak's position is in line with the previously published C 1s data for various systems containing the C–OH group ranging 291–291.5 eV, as mentioned in the Introduction, including the main peak of glucose C–OH centered at 291.5 eV.³¹ On the other hand, the modeled spectrum for the B tautomer exhibits discrepancies when compared to the experiment. With the positions of the smaller and main peaks at 293.4 eV and 291.6 eV, respectively, the energy separation between them is too small. Moreover, as the main peak is slightly broader, the relative intensities of the main and smaller peaks differ from the experiment. Therefore, we confirm that the A tautomer prevails in solution, and subsequent deprotonations will be considered for this structure.

Let us now focus on a singly deprotonated form of vitamin C, with the deprotonation site assigned to the C3–OH site by NMR.³⁸ The pH = 7 PE spectrum (panel B, black line) exhibits similar main and C1 peaks, but their positions have clearly changed with respect to pH = 2, with their maxima at BE = 291.4 eV and BE = 293.0 eV, respectively. Moreover, a shoulder at BE = 290.4 eV appears, originating from the C2 1s electron according to our calculations (Table 1). These observations indicate that vitamin C exists in a different form at pH = 7 compared to pH = 2; the good match with theory indicates that, indeed, a singly deprotonated form is present, as discussed in the following. The ascorbic-acid molecule has four –OH groups (at carbons C2, C3, C5, and C6) that could, in principle, deprotonate at relatively low pH (Fig. 2). Therefore, we modeled spectra for all four hypothetical acid–base forms using the cluster-continuum solvation model; results are shown in panel B of Fig. 3 for C2 (green), C3 (red), C5 (blue), and C6 (purple). When comparing the calculated spectra to the experiment, only one modeled deprotonation site (C3–O[−]) reproduces the experimentally observed features, with the additional shoulder at ≈290 eV being the most distinct one. Our calculation predicts positions of the main and the smaller peaks of 291.2 eV and



good agreement with the measured spectrum (Table 1). Thus, our approach directly enables us to uniquely assign the two deprotonation centers in the molecule to C2-O⁻ and C3-O⁻. Our conclusion is in accordance with previously published results from NMR.³⁸ To our knowledge, this is the very first time LJ-PES has been used to site-specifically probe double deprotonation acid-base sites. Although the double deprotonation of vitamin C has been previously probed by NMR, we highlight that LJ-PES augmented with theory can be used to derive the same structural information in this case, and in addition, promises to provide a plethora of complementary information, *e.g.*, on electronic structure, electronic decay channels, speciation or intermolecular interactions.^{28,29,89}

3.3 Fast and reliable *ab initio* interpretation of the experimental data

We now focus on the accuracy of our calculations. The so-far presented spectra were modeled using the maximum-overlap method based on a single structure for each protonation state. Therefore, the computations are inexpensive and relatively straightforward. Yet, they appear to be surprisingly accurate, as summarized in Table 1 and Fig. 5. All the peak positions are reproduced with an accuracy of 0.2 eV compared to the

experiment, which has its own uncertainty of ≈ 0.1 eV. The small inaccuracies in our computations are attributed to multiple approximations, as described in the Calculations section, inevitably accompanying any theoretical effort to describe complex disordered systems of solvated molecules. We can compare our results to the typical accuracy of the state-of-the-art approach based on the equation-of-motion coupled clusters with single and double excitations (EOM-CCSD). With a small set of various gas-phase molecules, the reported mean average error (MAE) for calculated C 1s BEs was 0.68 eV, or 0.24 eV after shifting the values to eliminate systematic errors.⁹⁰ For aqueous-phase glycine, the error was 0.05–0.22 eV when employing equilibrium averaging with an explicit solvent model based on EOM-CCSD with an effective fragment potential and solvent polarization correction.⁹⁰ Our results thus indicate that the computational framework based on the maximum-overlap method combined with a suitably selected DFT approach is a powerful and efficient method for modeling core-level ionization. Although one could argue that the accuracy is based on an empirical combination of the CAM-B3LYP functional with a sufficiently large basis set and on possible cancellation of errors, we recommend this approach for modeling core-level electron ionization when aiming for high precision for a relatively low computational price. Before enough experimental data are collected to extract general trends, the above combination offers a pragmatic tool for the interpretation of the experimental data.

The spectra modeled in this work using a single optimized



Fig. 6 Comparison of different theoretical approaches to model C 1s PE spectra of vitamin C, and to the experimental PE spectra (black lines in each panel). Spectra from a single geometry optimized to its energetic minimum ('single') and from an ensemble of 100 structures sampled from molecular dynamics ('ensemble') are presented. (A) Calculated for single deprotonation/measured at pH = 7. Two PCM cavity radii specifications ('UFF' and 'Bondi') were tested for this case. (B) Calculated for full protonation/measured at pH = 2. (C) Calculated for double deprotonation/measured at pH = 13.

single-structure and ensemble models, irrespective of the PCM cavity model. The ensemble model provides a slightly less accurate (compared to the experiment) peak position in this particular case. While the nuclear-ensemble approach is an approximation, we attribute the worse agreement with the experiment to the insufficiency of our molecular dynamics used for the sampling. Particularly, we used the QM/MM method with a QM zone containing the ascorbic-acid molecule and an MM zone containing solvating water molecules. Thus, we interpret the discrepancy as an insufficient description of the explicit solvent structure around the vitamin C molecule. This claim is further supported by the spectrum of the fully protonated form in panel B of Fig. 6, where no explicit water molecules from QM/MM dynamics were used and where the 'single' and 'ensemble' spectra match in both peak positions. In fact, both are virtually identical, confirming that the single geometry is a good representation of the system distribution. Consequently, a single-structure spectrum based on optimization to the energetic minimum can provide a more reliable result in some cases, such as for the singly deprotonated form discussed above.

In panel C of Fig. 6, the results for the doubly deprotonated form of ascorbic acid are shown. Although the position

time, the method has been extended to a double-deprotonation case, demonstrating the ability to selectively probe two acid-base centers simultaneously. This enabled us to identify the two deprotonation sites, C2-OH and C3-OH, in the double-deprotonated form of vitamin C in a highly alkaline solution.

These results are consistent with previous findings based on NMR spectroscopy. The two approaches thus provide comparable structural information. As NMR sometimes suffers from structural misassignments,^{22–25} there is room for the development of complementary structure-sensitive techniques. Furthermore, LJ-PES provides additional advantages as it simultaneously captures the full electronic structure and reflects molecular interactions, *e.g.*, with the neighboring solvent molecules.²⁸ Note also that a single LJ-PES measurement can probe the structure from the perspective of different atomic species (*e.g.*, carbon and nitrogen) that can be helpful in the elucidation of complex structures. In the present case, probing the oxygen sites would be of little use due to the signal overlap with the aqueous solvent's oxygen. The LJ-PES technique can be conveniently expanded to studying air–water interfaces by varying the photon energy and thus the probing depth,⁹² exploring, *e.g.*, specific acid–base behavior and speciation at the interface, relevant for atmospheric chemistry.

An interesting phenomenon observed in the present study is that deprotonation affects BEs of core-level electrons of an atom that is a few chemical bonds away from the deprotonation site. This may be surprising, considering the enormous ability of water to screen the electrostatic effects.⁹³ Our observation is promising for a possible application of multivariate analysis techniques to the measured data to reconstruct the full molecular structure from LJ-PES.

We have presented an efficient computational approach to model C 1s photoelectron spectra in aqueous solution. It is based on a single optimized geometry and employs the maximum-overlap method with the CAM-B3LYP functional. With this, we achieved an accuracy of 0.2 eV for the modeled BEs. The computational protocol is inexpensive and relatively straightforward. Therefore, we recommend this approach as the first choice for calculating core-level BEs in aqueous solutions.

The high accuracy of the computational protocol is in line with our previous studies. Note that the calculated BEs are close to the experiment on an absolute scale. This finding is somewhat surprising in the present case for two reasons. First, the deprotonated forms of the ascorbic acid contain an O^- group with a highly concentrated charge. For calculations of the valence region, such a situation would usually require the inclusion of explicit solvent molecules in a large zone around the site.⁵⁰ Second, the same computational treatment is required when dealing with multiply charged anions.⁶² In the present case, correct core-level energies are reproduced even with a minimalistic model assuming just a dielectric approximation of the environment and a few explicitly treated solvent molecules.

available in the ESI.† The raw data relevant to this work has been deposited at DOI: 10.5281/zenodo.10706227.

Conflicts of interest

There are no conflicts to declare.

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