NEXAFS Chemical State and Bond Lengths of p-Aminobenzoic Acid in Solution and Solid State

NEXAFS Chemical State and Bond Lengths of p-Aminobenzoic Acid in Solution and Solid State

J S Stevens[1], A Gainar[1], E Suljoti[2], J Xiao[2], R Golnak[2], E F Aziz[2,3], S L M Schroeder[4,5]

[1]School of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
[2]Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq), Helmholtz-Zentrum Berlin für Materialien und Energie, Albert Einstein Strasse 15, 12489 Berlin, Germany
[3]Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
[4]School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK
[5]DIAMOND Light Source Ltd., Chilton, Didcot, OX11 0QX, UK

E-mail: joanna.stevens@manchester.ac.uk; s.l.m..schroeder@leeds.ac.uk

Abstract. Solid-state and solution pH-dependent NEXAFS studies allow direct observation of the electronic state of para-aminobenzoic acid (PABA) as a function of its chemical environment, revealing the chemical state and bonding of the chemical species. Variations in the ionization potential (IP) and 1s π* resonances unequivocally identify the chemical species (neutral, cationic, or anionic) present and the varying local environment. Shifts in σ* shape resonances relative to the IP in the NEXAFS spectra vary with C−N bond length, and the important effect of minor alterations in bond length is confirmed with nitrogen FEFF calculations, leading to the possibility of bond length determination in solution.

1. Introduction

Through X-ray absorption and emission spectroscopies, the chemical, electronic and structural properties of organic species can be investigated. The nature of solution species and their interactions can play an important role in the activity of biological systems [1] and in the structural outcome and therefore properties of crystallization products [2]. Near-edge X-ray absorption fine structure (NEXAFS) measurements allow direct observation of the electronic state of *para*-aminobenzoic acid (PABA) as a function of its chemical environment [3]. While the IP and π* resonances are characteristic of the species and related to their chemical and electronic nature in the solution and solid state, the dominating influence of bond length on the σ* shape resonance proposed from experimental data is here investigated with FEFF calculations, exploring the ability and sensitivity of measuring bond lengths.

2. Methods

2.1. N K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Solid-state partial electron yield (PEY) NEXAFS measurements were performed on the U7a beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY with the sample at 54.7°, a 600 l/mm monochromator grating, and an entrance grid bias of -150 V [3]. Spectra were normalized by the simultaneously recorded total electron yield signal from a gold-coated, 90% transmission grid in the incident beam (I_0), and the monochromator energy scale was calibrated using the 400.6 eV 1st π* of a titanium nitride grid. Solution-state partial fluorescence yield (PFY) spectra were recorded using the liquid microjet of the LiXEdrom endstation at the U41-PGM beamline of the BESSY II synchrotron at Helmholtz Zentrum Berlin (HZB) using an 18 μm diameter glass nozzle with 0.6 mL min^{-1} flow rate [3]. Beamline energy calibration was performed with N_2 gas (total electron yield X-ray absorption spectroscopy 1s 2p π transition). Peak fitting and normalization were performed using the Athena software [4,5], with arctan steps for the ionization potentials (IPs, edge steps) and Gaussian functions for the peaks.

2.2. FEFF calculations

FEFF8.2 [6] was used to simulate the * shape resonance in the N K-edge NEXAFS for a geometry optimized monomer of non-ionic PABA. The SCF (7.0), XANES (4.0), and FMS (10.0) cards were used, and the calculated data were rigid shifted by +2.3 eV. To identify the influence of the C–N bond length, the C–N bond length of α-PABA was increased by 0.002-0.1 Å relative to the equilibrium value for the non-ionic monomer.

3. Results and Discussion

Nitrogen K-edge NEXAFS measurements reveal variations for the PABA species in both the solid state and in solution (Figure 1). Characteristic spectra are obtained for the different chemical species (non-ionic, cationic, anionic) present in solution with variation in pH, with a distinctive electronic signature for the cationic form following the change in nitrogen protonation state (NH_2 to NH_3^+). Shifts in the ionization potential (IP, edge step) and 1s π* resonances unequivocally identify the chemical and electronic nature of the species present [3,7]. Further slight shifts and intensity variations are observed for the impact of differing local environments and interactions for the three non-ionic species investigated (α- and β-crystalline forms and the solutions species in methanol).

The energy of the σ* resonance associated with the C−N bond relative to the IP also varies across the series (term value δ_{C-N}, Figure 1). The decrease in δ_{C-N} appears to correlate well with successively longer C−N bond lengths reported by X-ray diffraction (XRD) for the solid-state (Table 1, $y = -39.664x + 61.133$) [3]. This relationship can then be applied to the NEXAFS data, using it to provide an indicator of bond lengths for PABA species in solution.

Table 1. N K-edge NEXAFS features and bond lengths [3].

	δ_{C-N} / eV	ê δ_{C-N} / eV	XRD C−N / Å	XRD lengthening C−N / Å	NEXAFS C−N / Å[b]
Non-ionic α-PABA	6.31	0	1.379(2)	0	1.382
Non-ionic β-PABA	5.49	-0.82	1.408(3)	0.029	1.403
Anionic pH 11	5.40	-0.91	1.410(2)[a]	0.031	1.405
Non-ionic Methanol	5.19	-1.12	/	/	1.411
Cationic pH 1	3.16	-3.15	/	/	1.462
Cationic HCl salt	3.05	-3.26	1.4626(5)	0.0836	1.464

[a] C−N bond length from the hydrated Na salt shown for comparison
[b] $y = -39.664x + 61.133$ for linear relationship between δ_{C-N} and XRD C−N/Å [3].
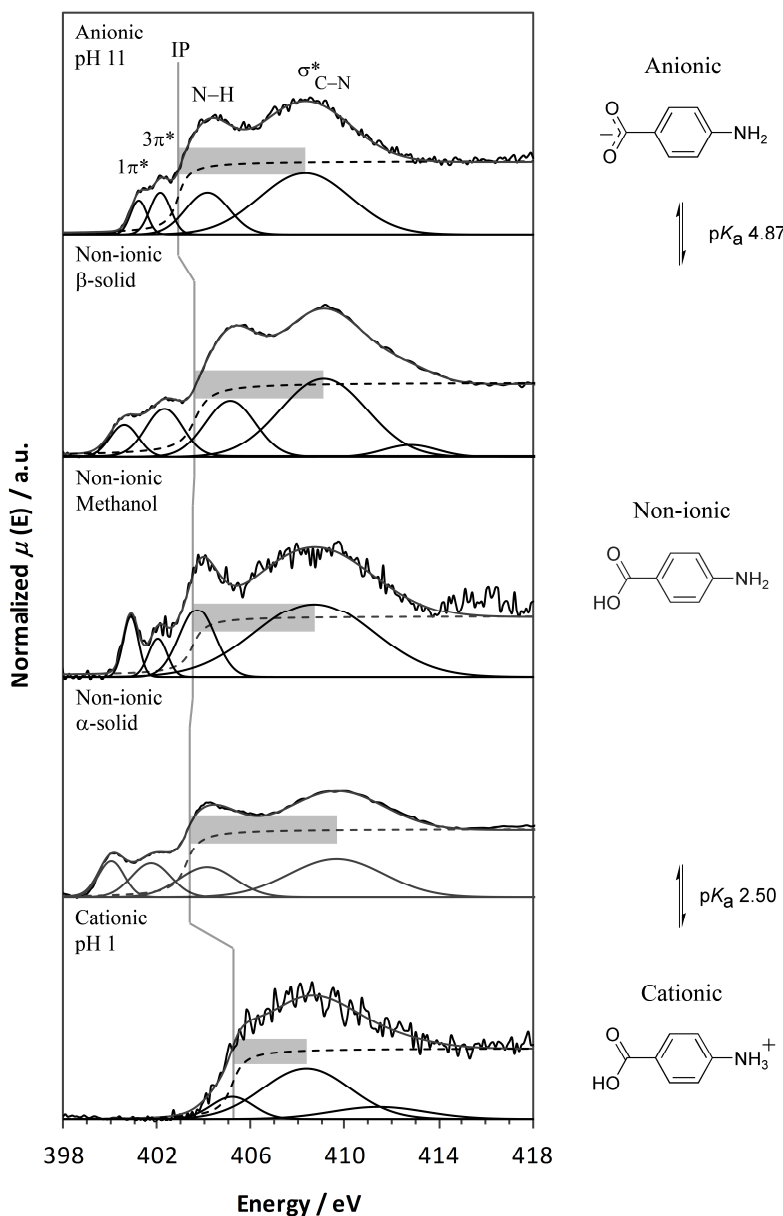
Figure 1. Nitrogen K-edge NEXAFS for anionic, non-ionic, and cationic PABA species in the solid and solution state, with the IPs marked by grey lines and the magnitude of the term value δ_{C-N} highlighted by grey boxes (adapted under CC BY license [3,7]).

To further investigate the impact of the C−N bond of PABA on the nitrogen NEXAFS, FEFF calculations were performed. Using an optimized non-ionic monomer as input, only the C−N length was varied, keeping all other parameters constant. This enables the effect of the C−N bond length to be isolated from other changes occurring between the species.

The C−N length was initially extended by 0.1 Ångstroms (Å), where a clear alteration and decrease in σ* energy of almost 2.5 eV is observed relative to the IP (ê δ_{C-N}, Figure 2). The changes in C−N bond length in practice are smaller than 0.1 Å, ranging from 0.002 to 0.08 Å for the different PABA species (Table 1). Smaller increments were therefore tested, with lengthening by 0.03 Å (to mimic that occurring on moving from non-ionic α-PABA to β- or anionic PABA) resulting in a decrease in

energy by around 0.8 eV (Figure 2). This compares favourably with experimental NEXAFS, where a 0.82-0.91 eV change occurs (for cationic species, underestimation of FEFF ê δ_{C-N} values may be related to the alteration in electronic structure and geometry accompanying the positive charge on N, bent NH_2 tetrahedral NH_3^+). The extreme sensitivity is further demonstrated for the case with just 0.005 Å longer C−N (Figure 2), and even the small shift occurring with 0.002 Å lengthening is observable, showing that even relatively subtle variations have a noticeable influence. The results suggest that bond length variations should be quantifiable to a precision of approximately 0.01 Å.
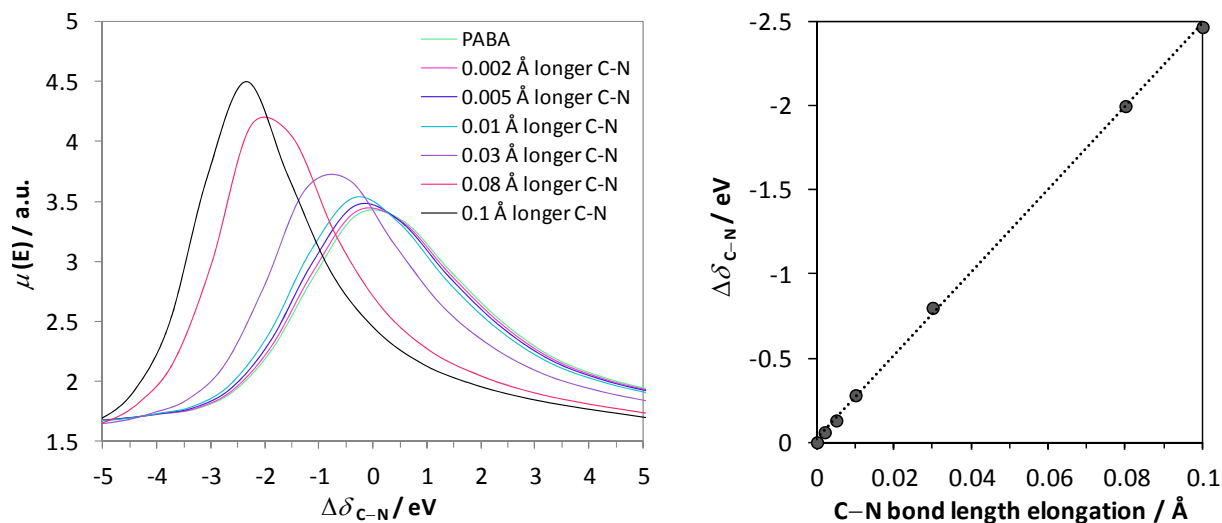

Figure 2. FEFF calculations for the nitrogen K-edge NEXAFS of PABA, demonstrating the effect of lengthening the C−N bond on the σ* energy relative to IP (δ^*_{C-N}).

4. Conclusions

Nitrogen NEXAFS acts as a chemical and structural indicator for PABA, identifying the chemical species present in both the solid-state and in solution as well as providing a measure of C−N bond length. The ability to detect even minor variations in structure is verified by the FEFF calculations through incremental variation of bond length, with changes from as little as 0.002 Å alteration visible. NEXAFS can then potentially provide bond lengths for solution (or amorphous) species, such as demonstrated with PABA, and the combination of experiment and calculations is particularly strong.

References

[1] Chatterjea M N and Shinde R. 2012 *Textbook of Medical Biochemistry* (New Delhi: Jaypee Brothers Medical Publishers (P) Ltd.)
[2] Davey R. J., Schroeder S L M, and ter Horst J H 2013 *Angew. Chem., Int. Ed.* **52** 2166-2179
[3] Stevens J S, Gainar A, Suljoti E, Xiao J, Golnak R, Aziz E F and Schroeder S L M 2015 *Chem. - Eur. J.* **21** 7256-7263
[4] Ravel B and Newville M 2005 *J. Synchrotron Radiat.* **12** 537-541
[5] Newville M 2001 *J. Synchrotron Radiat.* **8** 322-324
[6] Ankudinov A L, Ravel B, Rehr J J and Conradson S D, 1998 *Phys. Rev. B: Condens. Matter Mater. Phys.* **58** 7565-7576
[7] Stevens J S, Seabourne C R, Jaye C, Fischer D A, Scott A J and Schroeder S L M 2014 *J. Phys. Chem. B* **118** 12121-12128