

# Near edge X-ray absorption and emission of cyanates and thiocyanates

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(Dated: September 20, 2022)

The analysis of the electronic structure of selected cyanates and thiocyanates at the nitrogen K edge is presented in this work. Using high-resolution X-ray spectroscopy with calibrated energy scales and the access to absolute radiation dose induced damage in light elements, reliable and reproducible experimental results were achieved. In addition, theoretical modeling with first-principle calculations based on the Bethe-Salpeter equation for the excited-state interactions is used to interpret the experimental results obtained with X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) measurements.

## I. INTRODUCTION

The electronic structure of a chemical compound depends on the atoms involved as well as their respective distances and coordination geometry. Previously, the electronic structure of ionic crystals with molecular sub-components, e.g.  $\text{LiNO}_3$  [1] and  $\text{NH}_4\text{NO}_3$  [2], have been investigated by comparing experimental near-edge x-ray absorption and emission spectroscopy results with first-principles calculations. This paper continues this exploration by examining ionic crystals whose anions have a linear structure. The linear structure of the compounds provides the opportunity to study next-neighbor and next-to-next-neighbor interactions in crystal structures and their influence on the electronic structure. We analyze cyanates  $\text{CNO}^-$  and thiocyanates  $\text{SCN}^-$  with different metal cations using X-ray spectroscopic measurements to elucidate their electronic structure.

The electronic structure of cyanates and thiocyanates has been studied in the past using both X-ray absorption and infrared spectroscopy [3, 4]. Moderate to high energy resolution X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), with typical energy resolving powers  $E/\Delta E$  up to a few thousand, are powerful tools for probing the electronic structure of compounds. XES and XAS are used to analyse transitions involving both the occupied states [5, 6] and unoccupied states [7, 8], respectively. In addition, resonant inelastic X-ray scattering (RIXS) allows for a simultaneous investigation of both states, therefore providing supplementary information on energy dependencies and distributions of specific spectroscopic features.

Using well-known and calibrated instrumentation, reliable experimental data regarding the incident and emitted photon energies and the incident beam power, which is then used for comparison with theoretical data based on the Bethe-Salpeter equation (BSE) approach [9], is provided. The BSE approach is a first-principles method whose only truly free parameters are the positions of the

atoms in the structure being simulated. The excited-state interactions are included explicitly on top of the ground-state band structure. The mix of extended, ionic systems with small linear molecule constituents provides a good test case for these kinds of theoretical calculations.

The experimental results achieved with at the N K edge are interpreted using *ab initio* calculations with the OCEAN code [9, 10]. The systematic study of model systems presented here allows for a detailed comparison between experimental and theoretical data by focusing on a single element, in this case the nitrogen atom, and using the same set of calculation parameters except for the crystal structure. In this work, the aim is to provide a better model-based understanding of XAS and RIXS measurements using the OCEAN code and the BSE approximation. Furthermore, the investigation with synchrotron radiation requires the minimization of radiation damage [11]. Several methods for mitigating radiation damage are assessed in this work and a threshold for dosage is established for  $\text{NaOCN}$  and  $\text{NaSCN}$ .

Recent publications on XES and XAS of iron sulfur compounds [12] and titanium oxides [13] have already shown the discrimination capabilities and validation potential of calculations when comparing experimental and theoretical findings. In addition, the prediction capabilities of the OCEAN code have been shown in the RIXS analysis of various nitrogen compounds [2, 14, 15].

## II. EXPERIMENTAL SETUP AND MEASUREMENT PROCEDURE

### A. Experimental method

The experiments were conducted at the plane-grating monochromator (PGM) beamline [16] for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at the electron storage ring BESSY II. The beamline provides tunable linearly polarized undulator radiation in the soft X-ray range with photon energies between 78 eV and 1860 eV with high spectral purity and photon flux.

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For X-ray absorption measurements the induced fluorescence radiation is detected with a silicon drift detector (SDD) with a known spectral response behavior and efficiency [17, 18]. The near-edge X-ray absorption fine structure (NEXAFS) measurements around the N K edge were performed at an incident and takeoff angle of  $\theta = 45^\circ$  [19]. The incident photon flux is determined with a calibrated diode. The samples were inserted in an ultra-high vacuum environment allowing for the use of soft X-ray radiation.

The RIXS data has been recorded using a wavelength-dispersive spectrometer (WDS) [20–22]. The incident and takeoff angles of the fluorescence radiation is detected with a charge coupled device (CCD) detector positioned on the Rowland circle which is defined by the employed grating. The optical source is defined by means of an entrance slit which is also positioned on the Rowland circle between the grating and the sample. The resolving power of the spectrometer was set to  $E/\Delta E = 800$ . Additionally, a vertical slit and a horizontal slit are placed between the entrance slit and the grating, acting as an aperture against stray light. The vertical slit collimates horizontally so that the detector is not illuminated outside of its active area in the non-dispersive direction while the horizontal slit restricts the illuminated area of the grating in the dispersive direction. This way the solid angle of acceptance of the WDS is defined. The compact design of the WDS ensures high-stability which allows an absolute calibration of the instrument [21] with respect to both its detection efficiency and response function. The presented work used the absolute calibration of the energy scale to ensure a good comparability of the results with literature – provided that the calibration concepts are comparable – and with theoretical calculations. The achieved spectral resolution was determined by recording the elastic scattering of the incident monochromatic undulator radiation from a boron nitride sample which was used to determine the response function of the spectrometer.

In order to ensure physically traceable, reliable, and comparable absolute values, both the incident as well as the emission energy scale were calibrated carefully. The excitation energy scale was calibrated using well-known vibrational resonances of gas phase  $N_2$  [23]. The emission energy scale of the WDS used for RIXS measurements was calibrated using the elastic scattering of boron nitride, thus transferring the beamline’s energy scale to the spectrometer.

Five different commercially available materials (Sigma-Aldrich) in powder form were analyzed: sodium cyanate (NaOCN), sodium thiocyanate (NaSCN), potassium cyanate (KOCN), potassium thiocyanate (KSCN), and copper thiocyanate (CuSCN). The copper cation, with its filled  $3d$  valence orbitals, yields a significantly different electronic structure compared to the alkali metals sodium and potassium. However, copper cyanate is not stable and has not been included. The samples were prepared in two different ways. The first set of samples was

pressed into pellets with 10 mm in diameter and approximately 2 mm in thickness. The other set of samples was pressed as a thin layer of grains into an indium foil. The pellets were used for the RIXS and XAS measurements whereas the samples pressed in indium foil were used to measure the sample current during XAS measurements to analyse surface effects and to collect electron yield measurements which are not affected by self-absorption.

## B. Radiation damage considerations

The measurement of light elemental compounds requires special care regarding radiation damage [11, 24, 25]. Each X-ray emission spectrum measured at a specific incident photon energy is recorded during a 20-minute measurement time. To reduce any possible influence thereof the sample positions were changed between each spectrum during the RIXS measurements. Nevertheless, to evaluate the effects of synchrotron radiation in the X-ray range on the cyanates and thiocyanates during this acquisition time in particular, repeated NEXAFS measurements on pellets and sample current measurements of compounds pressed in indium foil were conducted. Figures 1(a) and 1(b) show NEXAFS measurements ( $\Delta E = 0.25$  eV) at the N K edge with increasing values of the radiation dose on a selected sample spot. Repeated NEXAFS measurements of the thiocyanate show a stable behaviour indicating that the electronic structure of the sample is not changed with increasing radiation dose. However, measurements of the cyanates show a significant change of the fine structure. The first measurement shows one distinct peak at 400.5 eV incident energy, whereas the subsequent NEXAFS measurements indicate a splitting into two peaks with the peak at lower energies around 399 eV growing with increasing radiation dose and the main peak being shifted to higher energies around 400.75 eV. Figures 1(c) and 1(d) show NEXAFS measurements by means of the sample current which indicates Auger and photo electrons escaping from the surface of the sample. The advantage of measuring the sample current is that it is not affected by self-absorption. Indeed, the mean free path of electrons is in the low nm regime, probing only the near-surface region. Using this measurement one has to be careful, since additional surface phenomena like secondary ionization or plasmon loss effects may occur [26]. In addition, the surface chemistry may be different or contaminated in comparison to the bulk. The comparison of the measurement of the fluorescence line intensity and the sample current confirm the stability of the thiocyanate [Fig. 1(d)]. The cyanate sample current with a peak at 400.5 eV indicates that the radiation damage induced changes are not observed on the surface but rather in the bulk. Further analysis of the peak at 400.75 eV showed that the C-N bond is being broken, and  $N_2$  gas is build trapped in the bulk.

We conclude that due to the extended measurement

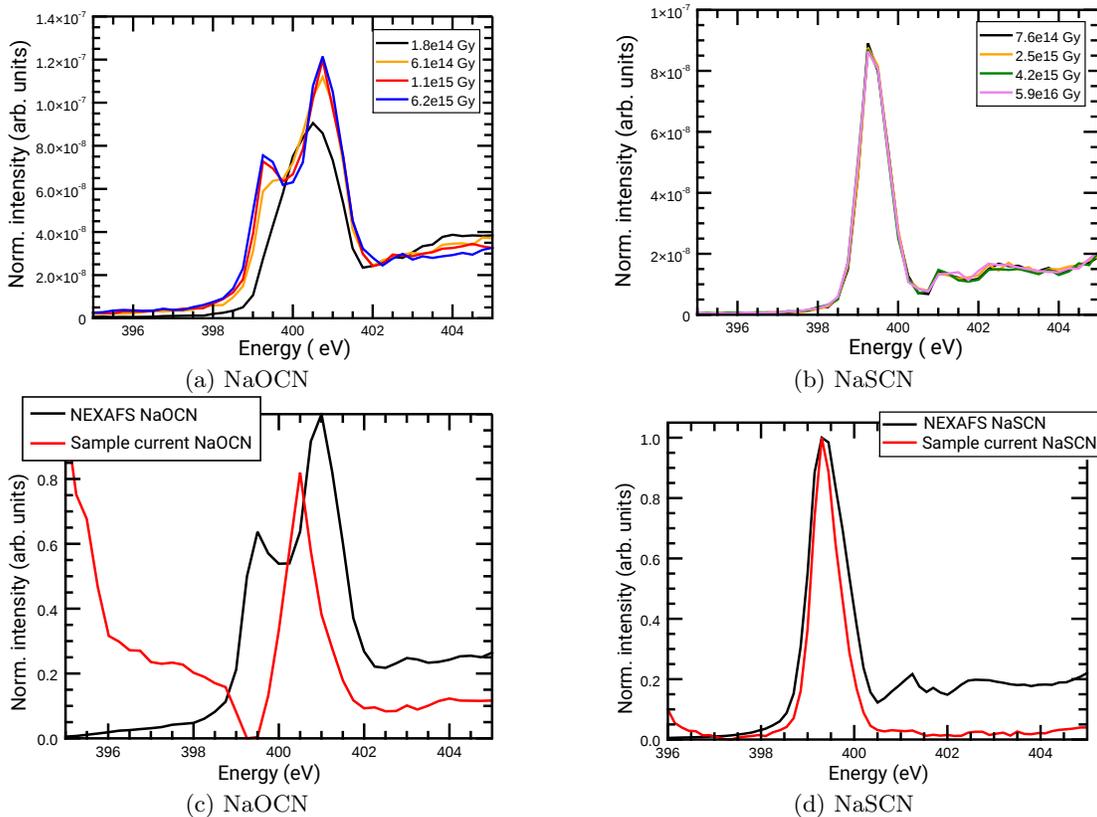


FIG. 1. Repeated NEXAFS measurements of NaOCN (a) and NaSCN (b) at the N K edge with increasing radiation dose. Comparison of the fluorescence line intensity (black) and sample current (red) measurements of NaOCN (c) and NaSCN (d) at the nitrogen K edge. For the sake of comparability, all spectra have been normalized to the maximum intensity which has been set to 1.

time required for the acquisition of a RIXS map, radiation damage free RIXS of the cyanates was not possible. For the cyanates only XAS results are presented in Section IV.

The results analysed in this work quantify the X-ray induced radiation damage to cyanates and emphasize the importance of radiation damage consideration and prevention need when analysing light elements with synchrotron radiation. For NaOCN a radiation dose above around  $1.8 \cdot 10^{14}$  Gy leads to radiation damage. Using this information, future measurements can be adjusted by constantly moving the sample during the exposure time, reducing the incident flux accordingly, or using efficient spectrometers that require less acquisition time.

### III. THEORETICAL MODELING

The OCEAN code was used for theoretical calculations throughout this work [9, 10]. OCEAN is a first-principles code for calculating core-level spectroscopy, including XAS and RIXS, using the Bethe-Salpeter equation (BSE) approach. We start with a ground-state calculation using density-functional theory (DFT) [27]. The BSE effective Hamiltonian describes interactions between the excited

photo-electron and the hole it left behind, using the occupied and unoccupied states from the initial DFT calculation as a basis. The strong excitonic attraction between electron and hole is screened by the rest of the electrons in the system. Here, QUANTUM ESPRESSO is used for the DFT calculations [28, 29]. The OCEAN input includes parameters like the atomic structure, photon excitation information, pseudopotentials for the DFT calculation, and specific convergence thresholds for the calculations. The pseudopotentials are taken from the PseudoDojo collection [30] and generated using the ONCVSP code [31].

One advantage of OCEAN is that a material can be simulated across different absorption edges and different techniques (e.g., XAS, XES, RIXS) using a consistent set of input parameters, thus simplifying comparisons between theory and experiment. Details on the calculations are as follows. Within the DFT calculation the quantum mechanical state of a many-electron system is calculated based on the local electron density. A fictional non-interacting system of fermions with an appropriate density-dependent potential is assumed. A common approximation is to neglect the electrons that are not participating in the chemical bonds, and thus in the calculation of molecule orbitals by dividing the electrons into core and valence electrons. The  $-Z/r$

| System | screening bands | cell volume ( $a_0^3$ ) |
|--------|-----------------|-------------------------|
| NaOCN  | 181             | 1198                    |
| KOCN   | 130             | 874                     |
| NaSCN  | 300             | 2090                    |
| KSCN   | 339             | 2407                    |
| CuSCN  | 75              | 476                     |

TABLE I. The number of bands used to calculate the screening of the core-hole potential is given by screening bands. The according unit cell volumes are shown in Bohr radius  $a_0^3$

ionic potentials are replaced by pseudopotentials that reproduce the correct valence electron behavior without explicit core-level electrons. The choice of the specific pseudopotential is crucial for a successful calculation. In this work norm-conserving pseudopotentials were used to employ the local-density approximation to the exchange-correlation functional. The structural input parameters [32] have been taken from the Materials Project database [33], with the exception of KOCN which was taken from experimental data [34].

The convergence parameters [32] that have been chosen for the calculations are summarized in the following. The plane-wave cutoff is used for the DFT calculation to truncate the basis and has been chosen for all compounds to be 150 Rydberg. The  $\mathbf{k}$ -mesh is the grid of crystal momentum points used for the calculation of the wavefunctions for the BSE and is chosen to be sufficiently high ( $k = \{8 \times 8 \times 8\}$ ) for the calculated spectra while avoiding excessive computational costs. The number of conduction bands included corresponds to the number of wave functions included up to some energy above the Fermi level in the Green's function and has been set to 150 for all compounds. The number of bands used to calculate the screening core-hole potential is given by the screening bands number given in Table I. For solving the BSE, the electron orbitals were down sampled onto a real-space mesh with a linear density exceeding 0.3 points per a.u.

#### IV. RESULTS AND DISCUSSION

We show the experimental and calculated results of the cyanates and the thiocyanates at the N K edge. Sec. IV A includes results of both the cyanates and thiocyanates whereas Sec. IV B shows the RIXS results of the thiocyanates. All spectra are normalized by the incoming photon flux and actual measurement time.

##### A. Results of XAS measurements

Comparing the obtained XAS experimental data (solid lines) with OCEAN calculations (dashed lines) with respect to peak positions, energy shifts, and peak forms shows good agreement for the studied materials, as can be seen in Figure 2.

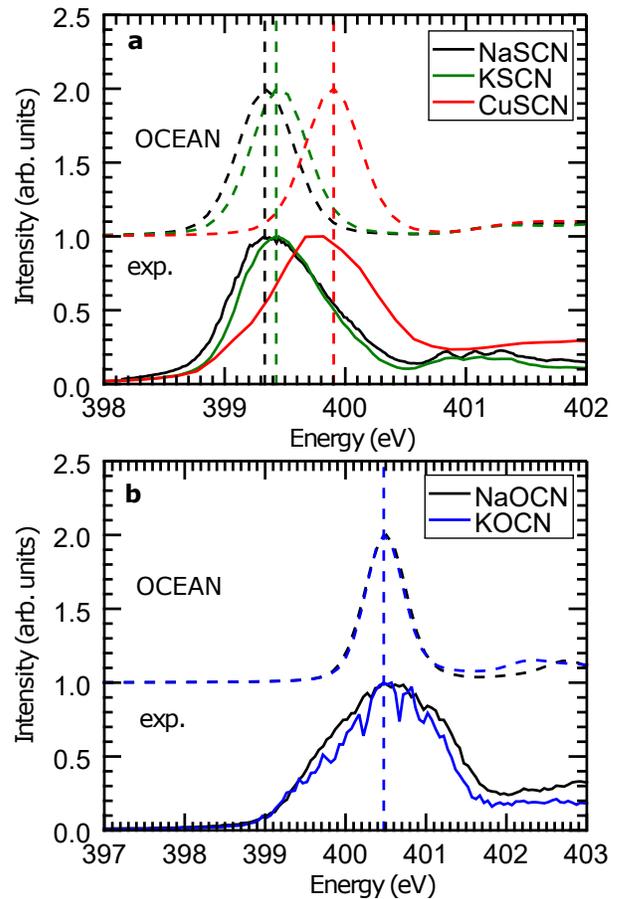


FIG. 2. The comparison of measured XAS spectra of the thiocyanates (a) and cyanates (b) at the N K edge with the calculated OCEAN data. For the sake of clarity, all spectra have been normalized to their respective maximum intensity and offset vertically.

The plots have been normalized to maximum intensity and the OCEAN results have been offset vertically for comparability. OCEAN does not calculate the absolute energy scale for X-ray excitations, but it does account for relative shifts between different chemical environments [2]. A single offset was determined by aligning the calculated and measured spectra for KSCN and was applied to all calculated spectra. We find good agreement between the experiment and calculated data for the peak positions associated with chemical shifts due to differing chemical bonds for all five compounds. Table II summarizes the relative positions between the compounds and position of KSCN. The given uncertainties are those from the fit of the features, which was conducted with an assumption of a Voigt profile for the peaks [32]. The core-hole lifetime effects at the N K edge are smaller than 0.1 eV, thus the Lorentzian width was set to be 0.1 eV while the Gaussian was determined to not be smaller than 0.22 eV according to the beamline resolution.

The observed differences in the peak position of the main exciton, e.g. chemical shifts, are the result of sev-

eral competing factors including the energy required to remove the nitrogen  $1s$  electron, the energy required to insert a conduction electron, and the excitonic binding of the electron–core-hole pair. Within OCEAN, relative changes in the core removal energy are determined by changes in the total Kohn-Sham potential experienced by the core electron and the adiabatic response of the valence electrons to the creation of a core hole, i.e., the dielectric screening [35]. The conduction band energies are taken directly from the DFT calculation, and the excitonic binding from the BSE. In the case of the five cyanates and thiocyanates investigated here, no single factor is responsible for the relative shifts. Changes to the cation simultaneously change the volume per formula unit as well as the ground-state electron density. An increase in the electronic density near the core will red shift the XAS, while a decrease in the volume will tend to increase the conduction band energies, blue shifting the spectrum.

In Figure 2(a) we show that the experimental spectra of NaSCN and KSCN differ in a chemical shift of the N- $1s$  level of about 0.1 eV which is represented correctly in the OCEAN calculation. The measured copper thiocyanate exciton peak position is higher than the NaSCN by 0.31 eV, while the calculated position is higher by around 0.44 eV. CuSCN has the least good agreement between calculated and measured shifts for the N K-edge exciton with a discrepancy of 0.13 eV (Table II). This may be related to shortcomings in the DFT treatment of localized orbitals like the Cu  $3d$  bands, which will be discussed later in Sec IV B. Nevertheless, this disagreement is only of the same order of magnitude as the estimated beamline energy resolution of  $\Delta E = 0.22$  eV ( $E/\Delta E = 1800$ ) [21].

Figure 2(b) with the comparison of the cyanates also shows agreement regarding the peak positions. During the measurement a significant effect of radiation damage was observed, which Section II B addresses in more detail. The cyanate’s NaOCN and KO CN bonds are highly sensitive to x-ray exposure. To reduce the impact of radiation damage on the experimental results the incoming photon flux was reduced (to around 8%) and the spectra in Figure 2(b) were taken on a fresh spot of the sample for each energy in the NEXAFS (20 s each spectrum). To take the spot-to-spot variations into account, the carbon fluorescence signal at 405 eV incident energy was recorded for each spot and used to normalize the NEXAFS.

All measured spectra show a difference in the width of the features. The broadening of features in a spectrum can be associated with a broadening due to core-hole lifetime, the resolution of the instrumentation, and vibrational disorder. The core-hole lifetime of nitrogen just above the K edge is about 0.1 eV and is included in the calculated spectra as a Lorentzian broadening. The resolution of the monochromator was applied to all calculated spectra as a Gaussian broadening. The resolution of the PGM beamline depends on the operation param-

| System | Shift (Exp.) | Shift (Theo.) | Exp.- Theo. |
|--------|--------------|---------------|-------------|
| NaOCN  | 1.10(7)      | 1.04          | 0.06        |
| KOCN   | 1.10(3)      | 1.04          | 0.06        |
| NaSCN  | -0.10(3)     | -0.11         | 0.01        |
| KSCN   | –            | –             | –           |
| CuSCN  | 0.31(8)      | 0.44          | -0.13       |

TABLE II. Summarized relative peak position shifts between four different compounds and the peak position of KSCN for the experimental data and calculated data as well as the difference between experimental and calculated shifts.

eters of the beamline [16] (monochromator  $C_{ff}$  parameter and exit slit width) as well as the respective energy. For the presented measurements in the energy range around 400 eV the resolution is estimated to be around 0.22 eV.

Still a discrepancy in the widths between the calculated and experimental data is observable which might be due to neglecting of vibrational disorder. OCEAN calculations are conducted for fixed unit cells. In reality the ions are vibrating around the equilibrium position [2]. Vibrational disorder can be incorporated as an ensemble of deviations from the regular supercell used in the calculation. These are generated by calculating the phonon modes of the system and creating snapshots of the band structure with a given probability distribution [2]. Figure 3 shows the comparison of experimental data to the OCEAN calculation on a unit cell and a calculation on a  $2 \times 2 \times 1$  super cell (containing 64 atoms). The theoretical calculation details for this calculation are described in Reference [2]. The comparison shows that the broadening due to vibrational disorder is significant but does not change the general shape of the spectrum. A discrepancy in the symmetry remains, since the experimental spectrum is still broader and asymmetric. Possible explanations for this are the use of the harmonic phonon approximation in simulating the vibrational disorder or the occurrence of vibronic coupling which is not included in the OCEAN calculations. In particular, the vibrational modes of the system are treated as having vanishing small energies as compared to the electronic excitations [36].

## B. Results of RIXS measurements

In Figure 5 the RIXS measurements of NaSCN and CuSCN are shown. Analogue to the XAS measurements, the results of RIXS measurements of KSCN are almost identical with the RIXS measurements of NaSCN and thus are not explicitly included in the following discussion. The cyanates are not stable during the exposure time required for a RIXS spectrum, and thus do not provide valuable information for a comparison with theoretical RIXS data. The RIXS measurements consist of a series of emission spectra at selected excitation energies which are varied around the absorption edge. The emission intensity is presented as the detected events on the CCD normalized to the incoming photon flux and expo-

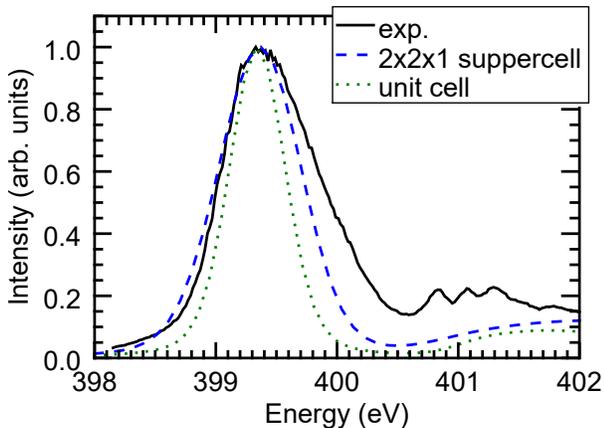


FIG. 3. The comparison of measured XAS spectra (black solid) of the NaSCN at the N K edge with the calculated OCEAN data on a unit cell (green dotted) and a super cell (blue dashed). For the sake of clarity, all spectra have been normalized to the maximum intensity which has been set to 1.

sure time, and then normalized to the maximum intensity for the sake of clarity.

The RIXS map can be deconstructed in two areas. First, the region below the emission energy around 395 eV emission energy is the fluorescence emission resulting from the creation of a hole in the valence band and is the main focus of our analysis. The second region is above 395 eV emission energy and shows both the expected elastic line, with emitted photon energies equal to the incident energy, as well as quasi-elastic feature with up to a few eVs of energy loss. This region will be discussed briefly at the end of this section.

The N K edge RIXS map of CuSCN in Figure 4(b) shows a deviation compared to the other NaSCN. Here, the feature energies shift in a more pronounced way, which is to be expected due to the significant electronic structure difference of the copper. The peak at around 390 eV emission energy does not occur in the CuSCN RIXS map and the peak at 401 eV incident energy is shifted to higher energies around 401.5 eV.

Figure 5 shows a comparison of the measured RIXS spectra with theoretically calculated spectra based upon OCEAN calculations for NaSCN and CuSCN. Shown are individual measured and calculated emission spectra at different excitation energies, offset vertically and normalized to the maximum intensity which has been set to one for clarity. The measured spectra (solid black lines) are normalized by the incoming photon flux and scaled to the maximum intensity recorded. The OCEAN calculated (dashed red lines) spectra are a result of a sum of all polarization directions of the incoming and outgoing photons due to the fact that the samples are not in an oriented crystal structure, thus no polarization direction is preferred. In addition, they are scaled to the maximum intensity for the sake of comparability. Since OCEAN does not calculate an absolute energy scale the

spectra are compared as functions of the energy loss  $\Delta\omega$  which is defined as the difference between the incident and emitted photon energy. The energy alignment with the experimental data was done by comparing the maxima of the feature at around  $-5$  eV of one X-ray emission spectrum. A broadening of 0.25 eV was applied to the OCEAN calculations to better match the resolution in the experimental data, which depends on the pixel size of the CCD camera, the resolving power of the grating, and the energy resolution of the beamline to some extent due to the fact that RIXS measurements are sensitive to uncertainties in the absorption channel. The overall resolving power of the spectrometer is represented through the response function of the spectrometer, which was determined using the measured elastic scattering and applied to the OCEAN calculated data.

The N K edge RIXS measurement of CuSCN in Figure IV B shows a deviation compared to the NaSCN RIXS measurement. Here, the feature energies shift in a more pronounced way, which is to be expected due to the significant electronic structure difference of the copper. The peak at around 390 eV emission energy does not occur in the CuSCN RIXS map.

The general observation is that the main features in NaSCN match in their spacing between the experimental and the calculated data, whereas, the CuSCN results show larger deviations. The high-energy peak at around  $-5.5$  eV for the NaSCN shows a good agreement with the OCEAN calculation. The same can be observed for the low-energy shoulder at around  $-10.5$  eV and  $-11.5$  eV, respectively. For NaSCN the feature at  $-7.5$  eV, which is dominant in the experiment, is suppressed in the OCEAN calculation. This feature also has larger changes in intensity in the OCEAN calculation than in the experiment. To understand the electronic structure provided by the RIXS analysis, a calculation of the projected density of states (PDOS) shown in Fig. 6 was conducted. We use the calculated PDOS to show how the 2p orbitals of each atom are distributed, and, in the case of the CuSCN, how the orbitals of the thiocyanate anion are strongly modified from what is expected for a free ion. Here, the PDOS of the contributing atoms are shown together with the experimental and OCEAN calculated X-ray emission spectra at 399.7 eV and 399.8 eV incident energy for NaSCN and CuSCN respectively. In the linear thiocyanate anion there is strong hybridization between the occupied orbitals of the S, C, and N, while the alkali cation contributes an electron via ionic bonding. From the calculated PDOS in Fig. 6(a), the nitrogen 2p contributes to three regions. Below  $-11$  eV is primarily S 2p with weak C and N mixing, while from  $-10$  eV to  $-9$  eV is primarily C and N, and at  $-7$  eV to  $-5$  eV is again dominated by the S with strong N mixing. For these features the position and weights of the calculated XES (grey) agree well with the measured XES (orange). However, the feature in Fig. 5 (a) at an energy loss of  $-7.5$  eV is clearly much stronger in the measured XES than in the calculated XES. Further, there is no corresponding feature in

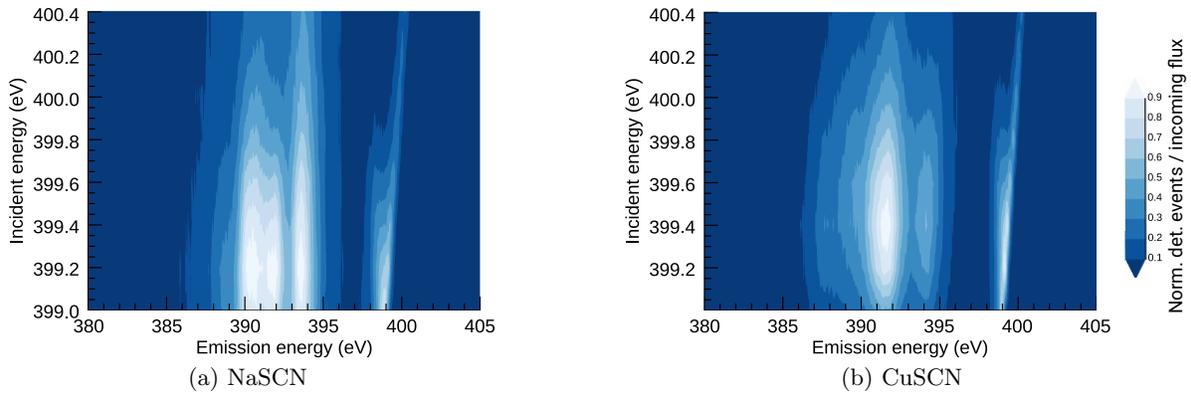


FIG. 4. RIXS measurements of NaSCN (a) and CuSCN (b) above the N K edge.

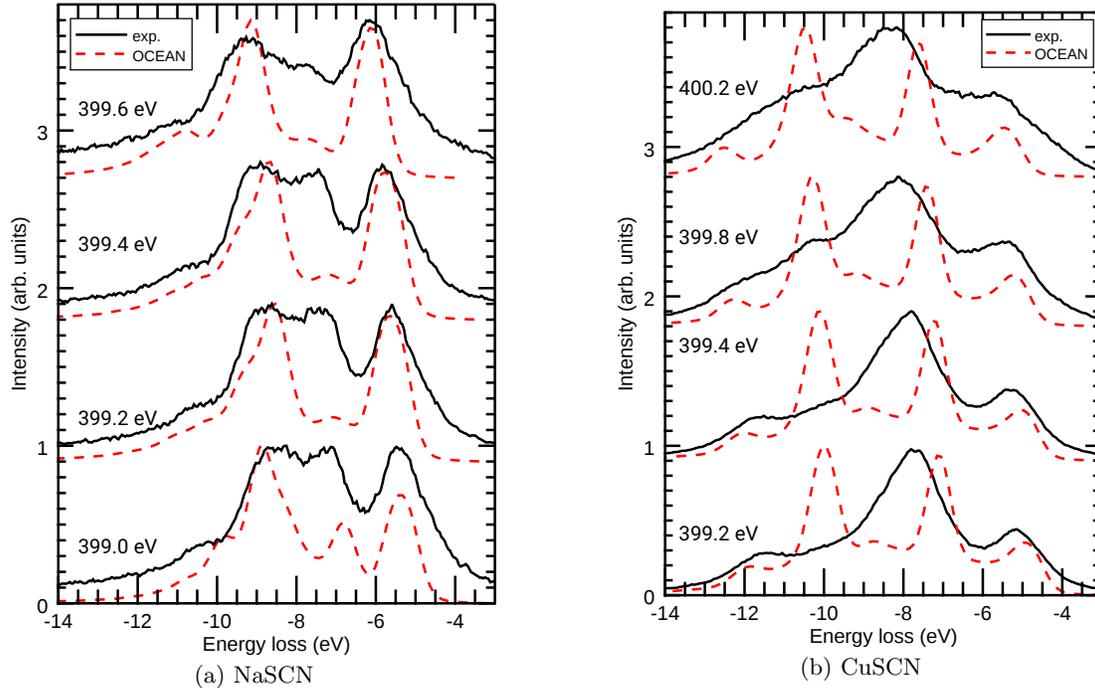


FIG. 5. Energy loss spectra at different excitation energies for (a) NaSCN and (b) CuSCN comparing experimental data (solid line) with OCEAN calculated RIXS spectra (red dashed line). Emission spectra at different excitation energies are offset vertically for the sake of clarity and labeled on the left-hand side by the initial excitation energy. Spectra have been offset vertically and normalized to the respective maximum intensity which has been set to one for the sake of clarity.

the PDOS. A comparison with XES measurements of  $N_2$  on a Ni-wafer from Petterson et al. [37] shows a peak at  $-7.5$  eV corresponding to the N-N bond. This is in alignment with Figure 2 (a) which indicates some  $N_2$  gas build up at around  $400.75$  eV absorption energy.

Fig. 5 (b) shows the comparison of measured and calculated RIXS spectra of CuSCN. The most intense peak at around  $-10.5$  eV in the CuSCN OCEAN calculation seems to be suppressed in the experimental data. However, the peak positions for the experimental and calculated data seem to match very well. This is summarized in Tab. III, where the peak positions were extracted by performing a deconvolution of the measured data with Voigt functions [32]. It appears that the discrepancy

in peak positions is less than within  $0.5$  eV. Cu  $3d$  orbitals may not be correctly treated by the DFT since there remains a difference in peak intensities. The incorrect relative energy of DFT calculations of filled  $d$ -bands has been noted previously [38, 39]. It is clear in comparing the PDOS between NaSCN and CuSCN (Fig.6) that the Cu  $3d$  state hybridize with the  $SCN^-$ , shifting peak positions and intensities and splitting the occupied states into additional groups. Changes to the energy of the Cu  $3d$  and especially to their spatial extent will correspondingly change the N  $2p$  orbitals and the relative peak strengths in the XES. In addition, we observe that the PDOS for NaSCN and CuSCN show a similar behavior around  $-9$  eV to  $-10$  eV, both showing

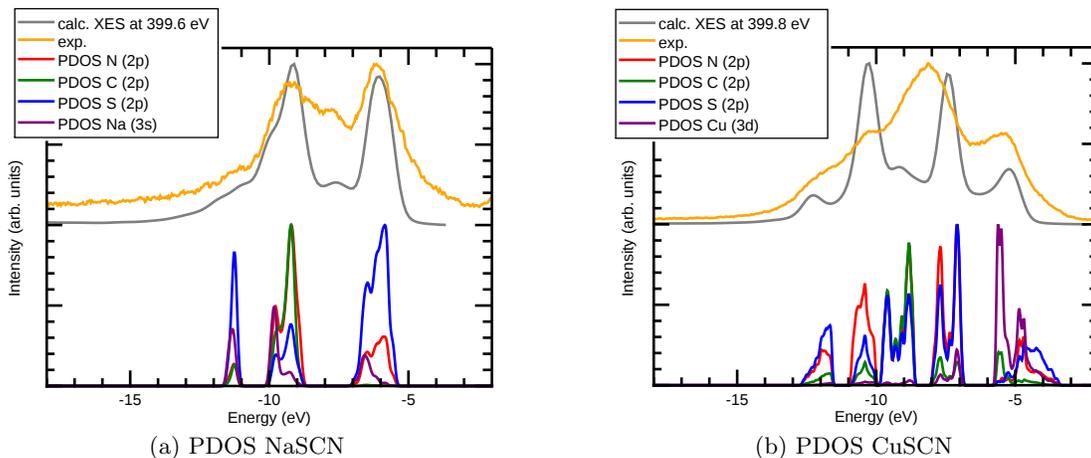


FIG. 6. Projected density of states for NaSCN and CuSCN compared to the according OCEAN calculated XES (grey) and experimental data (orange).

|   | OCEAN E pos. (eV) | Exp. E pos. (eV) |
|---|-------------------|------------------|
| A | -12.31            | -11.97           |
| B | -10.22            | -10.36           |
| C | -9.3              | -8.8             |
| D | -7.75             | -7.7             |
| E | -5.27             | -5.45            |

TABLE III. Comparison of peak energy positions as shown in Fig. 5 between OCEAN calculated and experimental data for CuSCN at 399.79 eV.

a hybridized orbital shared along the  $\text{SCN}^-$  ion. The main difference in the calculated RIXS spectra between NaSCN and CuSCN is that the contributions from this orbital are greatly reduced in the calculation, likely due to the influence of the copper.

Generally, the features in the experiment are broader than the calculated spectra despite the applied broadening from the response function. The OCEAN calculations were carried out on ordered unit cells. Calculating a disordered system might provide generally broader spectra (as seen in Fig. 3 for XAS) with slightly different feature ratios and suppressing of features like the one around  $-10.5$  eV in the CuSCN, but disordered RIXS calculations have not been carried out here due to the increased computational expense. Dramatic changes have been observed in systems with very light nuclei [15], but are not expected here, as Fig. 3 suggests for the absorption spectra.

The second region of the RIXS maps under investigation showing the quasi-elastic scattering emission has one feature that all five compounds have in common. This is the inelastic feature near the elastic scattering that can be observed for example in the NaSCN spectra at around 399.2 eV emission energy. The feature is resolved and is distinguished from the elastic peak of the excitation radiation. The emission energy of the feature changes and an energy loss can be observed. Likely these features are due to strong coupling to phonon excitations, which

can be observed in RIXS [40–42]. Such excitations are currently explicitly neglected in the computational approach we use here, and calculations of the influence of vibronic coupling on x-ray absorption and emission have been generally limited to molecular or localized systems.

## V. CONCLUSION

Using theoretical modeling with the OCEAN code and XAS as well as RIXS measurements we were able to provide an analysis of the electronic structure of selected cyanates and thiocyanates. We were able to theoretically and experimentally observe the effects of interchanging atoms within a class of inorganic salts built by cyanate and thiocyanate anions and metallic cations despite a strong effect of radiation damage in the cyanates. The same set of input parameters and energy offset was used to calculate all five compounds for the N-K edge in X-ray absorption and RIXS [32]. The results show discrepancies compared to the experimental data which could be narrowed down to shortcomings of the DFT treatment of the Cu 3d orbitals as well as the treatment of mixed covalent and ionic bonds. By comparing RIXS calculations with OCEAN and PDOS calculations with QUANTUM ESPRESSO we observed an overestimation of the Cu-N bond. However, we were able to provide results with very good agreement in the peak positions when comparing calculated and measured RIXS data as well as a good agreement in the XAS comparison.

With this work we continued the systematic investigation of the electronic structure of different crystals [1, 2] and showed the applicability of the OCEAN code to mixed covalent and ionic bonds. Vinson *et al.* [14] have shown that using the Bethe-Salpeter equation approach and incorporating disorder decreases discrepancies between experimental data and OCEAN calculations.

The measured RIXS spectra in Fig. 4 clearly show the importance of vibronic coupling which is responsible for

the low-loss features near the elastic line. Dynamic vibronic coupling to both the intermediate core-hole excited state and the final valence-hole state would likely influence the calculated XES, but such effects are not included in the current computational approach. One option for future work is calculations of the ground state potential energy surfaces and the Franck-Condon amplitude for the vibronic coupling as it has been proposed by Weinhardt et al. [42, 43]. We conclude that, when dealing with light compounds, computational models that include vibronic effects are crucial for reproducing x-ray spectra and a reliable investigation of the electronic structure.

## ACKNOWLEDGMENTS

Part of this research was performed within the EMPIR project AEROMET II. This project has received funding

from the EMPIR Programme co-financed by the Participating States and from the European Union's Horizon 2020 Research and Innovation Program. Certain commercial materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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