

Calibration method at the N *K*-edge using interstitial nitrogen gas in solid-state nitrogen-containing inorganic compounds

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The standard method of soft X-ray beamline calibration at the N *K*-edge uses the $\nu = 0$ peak transition of gas-phase N₂. Interstitial N₂ gas trapped or formed within widely available solid-state ammonium- and amine-containing salts can be used for this purpose, bypassing gas-phase measurements. Evidence from non-nitrogen-containing compounds (KH₂PO₄) and from He-purged ammonium salts suggest that production of N₂ gas is through beam-induced decomposition. Compounds with nitrate or nitrite as anions produce coincident features and are not suitable for this calibration method.

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1. Introduction

The ideal method for energy calibration of soft X-ray analysis at the nitrogen *K*-edge is the measurement of the vibrational peak positions of gas-phase N₂ with an in-line mounted gas cell. The vibrational manifold of the $1s \rightarrow \pi^*$ transition is well known from electron spectroscopy, and the $\nu = 0$ peak has an energy of 400.8 eV (Sodhi & Brion, 1984; Schwarzkopf *et al.*, 1999). Not all beamlines have facilities for gas-phase measurements, however, and in beam-time shifts where solid-state measurements are planned, set-up and use of the gas cell can be unwieldy and time-consuming.

Characteristic N₂ molecular vibrations in nitrogen-containing salts were observed during an investigation of natural reference compounds (Leinweber *et al.*, 2007). Also, trapped N₂ gas has been reported in the characterization of N₂⁺-bombarded alumina (Holgado *et al.*, 2003), and of compound semiconductors (Petravic *et al.*, 2006; Ruck *et al.*, 2004). The objective of this study was to conduct an assessment of suitable inorganic compounds that can be used for a simple alternative calibration method at the N *K*-edge using high-resolution scans over energies corresponding to N₂ gas.

2. Materials and methods

2.1. Reference compounds

The inorganic N-containing salts used as reference compounds are listed in Table 1. All reference compounds were pulverized with a mortar and pestle, affixed to double-sided conductive carbon tape (SGE, Toronto, Ontario, Canada) and mounted onto stainless steel sample discs. In addition, hydroxylamine hydrochloride and ammonium sulfate were dissolved in deionized water, purged with ultra-high-purity helium, evaporated under helium to remove existing N₂ gas, and pulverized and mounted as described above. Gas-phase photoabsorption N₂ measurements were obtained using a double

ionization gas cell with a 10 cm active pathlength in each chamber (Yates *et al.*, 2000) for comparison with N₂ vibrations measured in solid-state samples.

2.2. N *K*-edge XANES

Nitrogen *K*-edge X-ray absorption near-edge structure (XANES) spectra were collected using the spherical grating monochromator beamline 11ID-1 at the Canadian Light Source, Saskatoon, Saskatchewan, Canada. This facility delivers 10¹¹ photons s⁻¹ at the N *K*-edge with a resolving power ($E/\Delta E$) greater than 10000 (Regier, Krochak *et al.*, 2007; Regier, Paulsen *et al.*, 2007). Fluorescence yield (FLY) data were recorded using a two-stage multichannel plate detector that was operated in parallel with total electron yield (TEY) data collection through measurement of the drain current from the sample. High-resolution scans were taken using a step size of 0.01 eV over the expected range for N₂ gas, and of 0.1 eV for the remainder of the scan. Spectra were normalized to the incident flux using an in-line Au mesh which was refreshed by evaporation *in situ* prior to data

Table 1

Names, formulae, CAS (Chemical Abstracts Service) numbers and suppliers for compounds used in this study.

Compound	Formula	CAS number	Supplier
Ammonium chloride	NH ₄ Cl	12125-02-9	AnalaR
Ammonium phosphate, dibasic	(NH ₄) ₂ HPO ₄	7783-28-0	BDH
Ammonium phosphate, monobasic	(NH ₄)H ₂ PO ₄	7722-76-1	EMD
Ammonium sulfate	(NH ₄) ₂ SO ₄	7783-20-2	Fisher
Ammonium nitrate	NH ₄ NO ₃	6484-52-2	Sigma-Aldrich
Hydroxylamine hydrochloride	NH ₂ OH.HCl	5470-11-1	Chemservice
Potassium nitrate	KNO ₃	7757-79-1	EMD
Sodium nitrite	NaNO ₂	7632-00-0	Sigma-Aldrich
Potassium dihydrogen phosphate†	KH ₂ PO ₄	7778-77-0	Baker

† Ultra-high purity (99.8%).

collection. Data processing was carried out using the *Athena* software package (version 0.8.050). Data from at least two scans were averaged, and background-corrected by a linear regression fit through the pre-edge region followed by normalization to an edge step of unity.

3. Results and discussion

Fig. 1 shows FLY data of N *K*-edge XANES scans for the inorganic N-containing compounds studied, with panel (a) illustrating the energy region surrounding the vibronic structure of N₂ gas in detail, and panel (b) showing the full scan. Nitrogen gas vibronic structure is clearly evident in the reduced N-containing (*i.e.* ammonium- or amine-containing) salts that do not have an oxidized N anion. The $\nu = 0$ transition occurs at the same peak position in the solid phase as it does in the gas phase (Fig. 1a). The data of Chen & Sette (1989) show no significant shift in the peak position until the peak width broadens by over 100 meV, by which time a significant change in the overall shape has occurred. Provided there is a valley between the second and third peaks, we quantitatively estimate the accuracy to be within 100 meV. Peak widths, however, vary owing to lifetime reduction through solid-state mechanisms. This change correlates with the crystal lattice constant, and thus with confinement of N₂ gas within the solid phase. This has been discussed in detail with respect to compound semiconductors by Petravic *et al.* (2006).

The presence of nitrate (NO₃) or nitrite (NO₂) produces a feature at 401.7 eV, which is coincident with $1s \rightarrow \pi^*$ of N₂ gas, rendering these compounds less useful for calibration purposes. Although observed previously (Leinweber *et al.*, 2007), this feature remains unidentified. It should be noted, however, that this feature was not observed in previously published analyses of KNO₃ (Vinogradov & Akimov, 1998; Rodrigues *et al.*, 2007), suggesting that it may be a product of beam-induced decomposition. If this is the case, it is not likely to be decomposing to nitrous oxide (N₂O) or nitrogen dioxide (NO₂), as this feature does not match previously published spectra for these oxides of N (Gejo *et al.*, 2003; Adachi & Kosugi, 1995). Decomposition to NO, however, is observed here in NH₄NO₃, with vibrations corresponding to published results (Adachi & Kosugi, 1995; Yates *et al.*, 2000; Remmers *et al.*, 1993).

Certainly, atmospheric N₂ trapped within the solid phase would explain the occurrence of this feature, implying that the use of any inorganic salt would suffice as a calibration material. However, spectra obtained for N-free ultrapure potassium phosphate (dibasic) showed no evidence of N₂ gas vibrational structure (Fig. 1). In addition, we analyzed ammonium sulfate and hydroxylamine hydrochloride that had been dissolved, purged of N₂ and recrystallized under an ultra-high-purity helium atmosphere. These scans showed the presence of N₂ gas, matching those obtained for the unprocessed salts (data not shown). While it is beyond the scope of this paper to determine the mechanism of entrapment or production of interstitial N₂, these results suggest that it is derived from decomposition of the ammonium moiety. Indeed, for calibration purposes, the salt must contain ammonium- or amine-N to be of use.

TEY spectra for selected scans are shown in Fig. 2, with panel (a) illustrating the region encompassing N₂ gas within the full scan pictured in panel (b). Scans for all the ammonium-containing salts, except NH₄NO₃, showed similar characteristics; thus only data for (NH₄)₂SO₄ are presented here as a representative scan. The N₂ gas vibronic feature is suppressed in all TEY scans for all substances, and is absent from NH₄NO₃ and KNO₃. TEY (with an estimated penetration depth of <10 nm) is more surface sensitive than FLY (with an estimated penetration depth of 70–100 nm) (Frazer *et al.*, 2003;

Katsikini *et al.*, 1997). This suggests that the N₂ gas originates (*i.e.* is entrapped or produced) below the surface layer, and that any N₂ at/near the surface is removed in the vacuum chamber. Therefore, as a calibration method, TEY provides a less useful measure of absorption when compared with FLY. TEY data also revealed a stronger feature at 401.7 eV seen in KNO₃ and NaNO₂, indicating that, if this is a decomposition product, the mechanism of its formation is surface-sensitive.

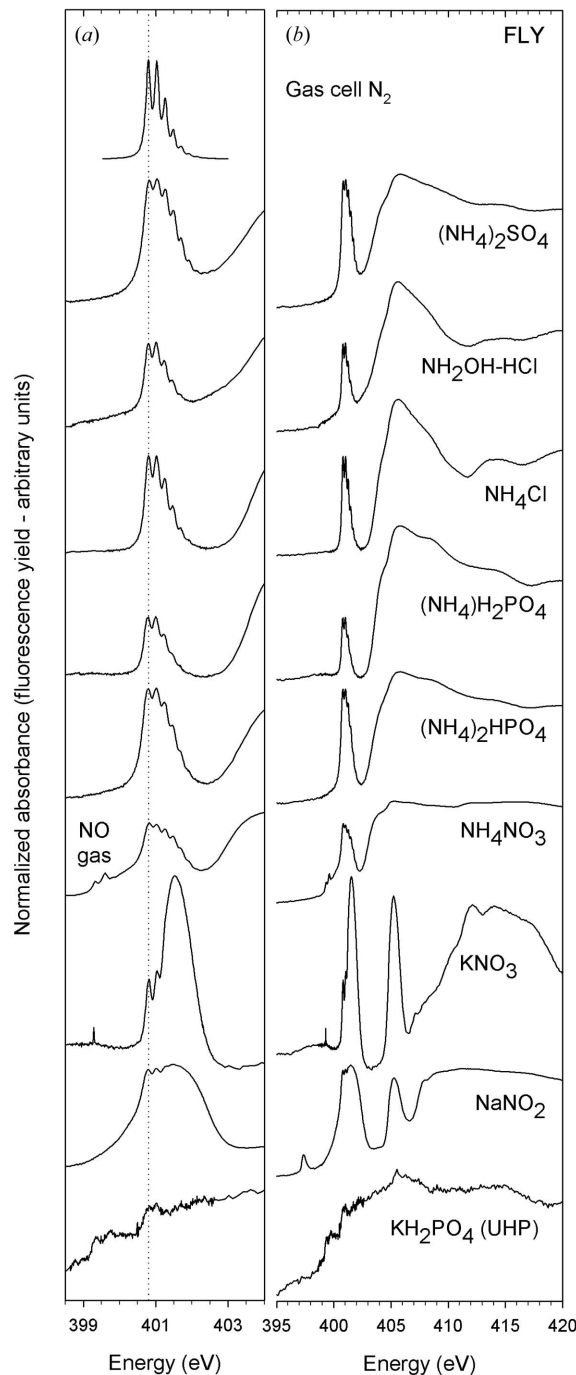


Figure 1 Nitrogen *K*-edge FLY spectra showing N₂ gas in the solid state of inorganic salts used in this study. (a) Detail of the high-resolution section, (b) full N *K*-edge scan. The dotted line corresponds to 400.8 eV, which is the $\nu = 0$ peak for the vibrational manifold of the $1s \rightarrow \pi^*$ transition for N₂ gas (Sodhi & Brion, 1984; Schwarzkopf *et al.*, 1999).

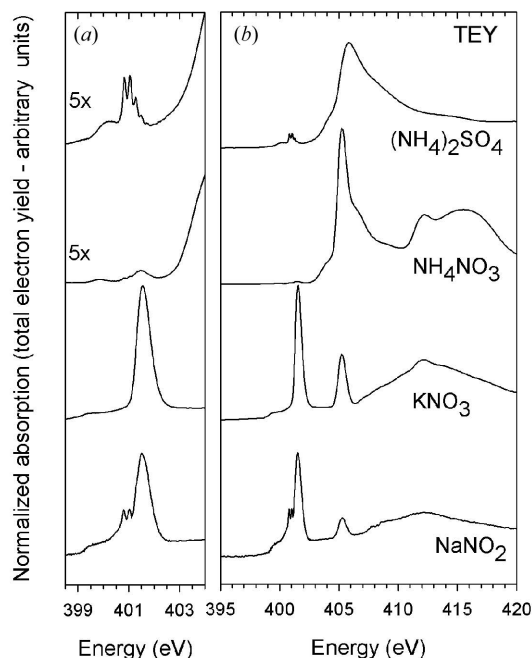


Figure 2
Nitrogen *K*-edge TEY spectra showing suppressed N_2 gas detection. (a) Detail of the high-resolution section, (b) full N *K*-edge scan. The spectrum for ammonium sulfate is representative of all spectra of ammonium- and amine-containing salts.

4. Conclusions

Interstitial N_2 gas contained within solid-state inorganic ammonium- and amine-containing salts can be used to quickly and accurately calibrate soft X-ray beamlines at the N *K*-edge without the need for gas-cell measurements. Dinitrogen gas contained within these solids may be generated *via* beam-induced decomposition. Other, as yet unknown, compounds may be produced if the anion is an oxidized N moiety such as nitrate or nitrite. Characteristic N_2 molecular features are observed more strongly with FLY, indicating formation/presence within the bulk material.

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