# 1s shake-up x-ray photoelectron spectrum of Na in NaCl and other Na salts

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Shake-up lines associated with the $Na^+[1s2p]3p$ atomiclike configurations in NaCl and several Na compounds have been identified in x-ray photoelectron spectra using commercial Al and Mg $K\alpha$ sources. Two clearly separated peaks in a ratio of about 1:2 split by 4.4 eV and with a binding energy of 56.6 and 61.0 eV greater than that of the 1s peak are observed. The possibility to perform a similar shake-up spectroscopy on heavier third-period elements for atomic and condensed-matter studies is addressed.

A great deal of information on electron correlation in atoms can be gained by studying excited state configurations with strongly interacting multiple core holes. Several spectroscopies are able to study double core-hole resonances of selected atoms in gaseous or solid compounds. X-ray absorption (XAS), x-ray photoelectron (XPS) or emission spectroscopies probe different aspects of the atomic excitation and provide complementary information. It is well known that in XPS spectra correlation effects produce satellites of the main core levels peaks associated to the "shake-ups" of weakly bound electrons.[1]

We will focus our attention on the single-photon excitations that create a 1s and a 2p hole occurring in neon and in third-period elements above a certain photon energy threshold. The 2p hole generates a nonspherical perturbation into the atom and interacts sufficiently with the 1s hole providing a complex phenomenology. The main features are, however, expected to be largely independent of the possible atomic ligands since relatively deep core states are involved. Indirect evidence for the formation of both $[1s2p]^1P$ and $[1s2p]^3P$ double hole configurations upon excitations is provided by the existence of the $\alpha'$, $\alpha_3$, $\alpha_4$ lines in x-ray emission spectra of Ne (Ref. 2) and third period atoms, including Na compounds.[3] Direct evidence for the occurrence of such a phenomenon came from the analysis of the 1s photoelectron spectrum of Ne.[4] A spectrum collected with laboratory equipment using a monochromatized Al K$\alpha$ photon source[5] showed a very complex shake-up structure including $2p \rightarrow np$ and $2s \rightarrow 3s$ shake-up lines. A more recent study[6] has brought evidence for autoionizing profiles in the latter transitions. However, the widest recent experimental evidence for the existence of the $[1s2p]$ double hole resonances has come from XAS experiments on molecules or solids containing third-period elements. Autoionizing resonances with asymmetric line shapes, superimposed to the absorption continuum due to the preceding $K$ edge, were observed in x-ray absorption spectra of Ne,[7] Si molecules,[8] P, S, and Cl compounds,[9] and Ar.[10] They have been assigned to atomiclike configurations of the type $[1s2p]np^2$ that generate three symmetry allowed $^1P$ states split into two groups by the hole-hole exchange interaction. At photon energies larger than those corresponding to the discrete resonances, transitions to continuum states in which the atom is left in the $[1s2p]np$ configuration occur. These are the shake-up channels associated with the $KL$ edge which have been shown to give an extra contribution to the absorption background of the order of a few percent of that of the main $K$ edge.[11]

The presence of the shake-up channels can be better evidenced looking at the photoelectron spectrum ejected by the sample than at its absorption spectrum but besides Ne,[5] direct evidence for the presence of shake-up channels in third-period atoms, which would be particularly interesting in light of the several XAS experiments,[7-10] is lacking.

The purpose of this paper is to present the results of an experiment performed on several Na compounds to detect possible shake-up channels associated with the contemporary excitation of the 1s and 2p electrons following the 1s photoelectron peak, in a binding energy scale, and to provide a preliminary peak assignment. A similar experiment has been carried out in parallel on MgO and MgF$_2$ by another group.[12] It should be noted that this kind of spectroscopy, performed with laboratory equipment is hampered by various intrinsic limitations. Clearly a high flux, tunable, monochromatized photon source would be particularly desirable, allowing to perform high-resolution energy-dependent experiments. Besides, with the usual laboratory Al K$\alpha$ radiation the double $[1s2p]$ hole can be generated only up to the Mg atom. In light of the developments of synchrotron radiation sources and monochromators, prototype experiments on laboratory machines, like the present investigation, are also useful to assess the general feasibility of the research.

X-ray photoelectron spectra have been recorded in an UHV chamber (base pressure of $2\times10^{-10}$ Torr) equipped with commercial photon sources (Al anode, $h\nu=1486.6$ eV and Mg anode, $h\nu=1253.6$ eV) and a hemispherical analyzer (the overall instrumental resolution was about 1 eV). The energy calibration was based on the gold photoline Au $4f_{7/2}=84.0$ eV. Samples have been chosen among the most common, UHV compatible, ionic compounds of Na, namely NaCl, Na$_2$SO$_4$, NaNO$_3$, Na$_2$HPO$_4$, Na$_2$CO$_3$, and NaHCO$_3$. XPS spectra have been measured in the extended range 1050–1160 eV of binding energy and in a

narrower energy interval 1118–1158 eV around the shake-up peaks with an improved statistics. In order to confirm the existence of the observed features the measurements on NaCl have been repeated on a different experimental apparatus equipped with an hemispherical analyzer and a monochromatized Al $K\alpha$ source.

The Al (monochromatized and not) and Mg $K\alpha$ photo-electron spectra for NaCl are presented in Fig. 1. Apart from unimportant differences in the background of secondary electrons due to the different kinetic energies for Al and Mg sources or different instrumental transmission functions, the three spectra are quite similar. The 1s core peak, followed by a large hump ($\approx$1090 eV) due to energy losses or shake-up excitations associated with the valence electrons, is clearly visible. This features have been already observed and discussed.[13] On the left-hand side of the spectra two weak features, superimposed on the tail of secondary electrons, which is more evident with the Mg $K\alpha$ source due to the lower kinetic energies, can be identified. The reproducibility of the results, that are independent of the photon energy and confirmed by the measurement with the monochromatized Al $K\alpha$ source, exclude any possible spurious origin for the two features.

Their binding energy is 60 eV higher than the 1s peak excluding any one-electron origin. Notice that the binding energy of the Na 2p electron in NaCl is about 30 eV, and around 30 eV higher in binding energy than the 1s peak a very weak feature can be seen. It is clearly associated with an energy loss edge due to the excitations of Na 2p electrons to the lowest conduction band states from the 1s core level photoelectrons. The relatively stronger features around 60 eV on the other hand have to be clearly identified with shake-up peaks associated with the contemporary excitation of the 1s and 2p electrons on the same Na atom.

A very similar behavior is observed in all of the other Na compounds. The shake-up energy regions, measured with Al $K\alpha$ radiation, are shown for comparison in Fig. 2. The energy scale $\Delta E$ represents the excess binding energy with respect to the 1s core peak of each corresponding spectrum. The shake-up spectra appears to be quite similar, probably because of the strong ionic character of the compounds. To a more refined level of analysis some differences in intensities and chemical energy shifts are detectable reflecting the influence of the chemical environment. The smallest $\Delta E$, associated with the highest intensity, are seen in the most ionic compound NaCl. NaNO$_3$ in comparison shows weaker shake-up peaks and a larger $\Delta E$ value. Similar chemical shift effects are found between MgO and MgF$_2$.[12] The intensity behavior can be qualitatively explained in terms of an increase of the overlap matrix element $\langle 2p|3p \rangle$ occurring in highly ionic compounds, similarly to what is observed in XAS spectra of S and Cl compounds.[9]

In Fig. 3 we show the NaCl shake-up spectra, collected with the two different photon sources, after a background subtraction effectuated with standard procedures.[14] The experimental signals are composed of two intense peaks labeled A and B followed by the weaker features C and D that have been identified with statistical significance.
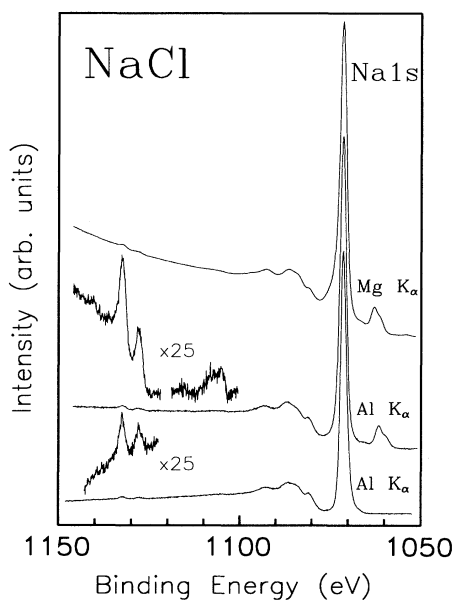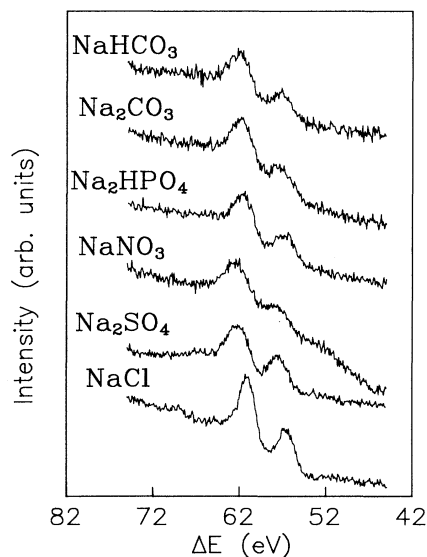


FIG. 1. X-ray photoelectron spectra of NaCl around the 1s core peak. From top to bottom the three curves refer to Mg $K\alpha$ source, Al $K\alpha$ source, and monochromatized Al $K\alpha$ source (where the $K\alpha_{3,4}$ component is suppressed). Apart from the different background of secondary electrons all the three spectra agree showing the presence of a weak doublet around 1130 eV of binding energy associated with the $2p \rightarrow 3p$ shake-up. The insets on top of the corresponding spectra report a 25 times magnified detail of the shake-up region. The other magnified inset in the 1100-1120 eV region shows the energy loss threshold around 1103 eV for 1s photoelectron that excite Na 2p electrons.



FIG. 2. Comparison of the Al $K\alpha$ XPS spectra of NaCl, Na$_2$SO$_4$, NaNO$_3$, Na$_2$HPO$_4$, Na$_2$CO$_3$, and NaHCO$_3$ in the $2p \rightarrow 3p$ shake-up region. The energy scale reports the excess binding energy with respect to the 1s peak. The intensities have been scaled to the relative 1s peaks and are directly comparable. The two peaks separated by $\approx$ 4.5 eV are clearly visible in all compounds.
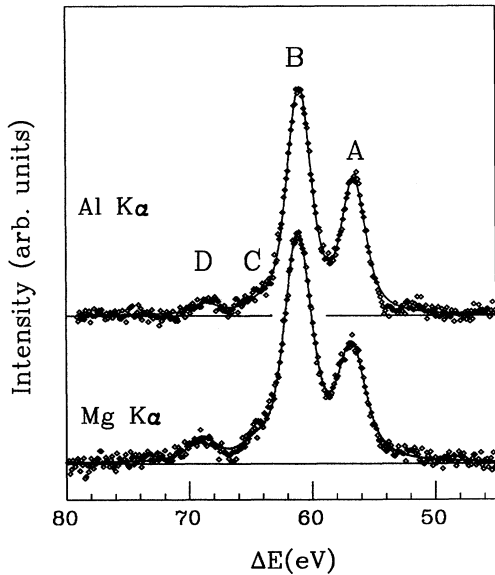
FIG. 3. Comparison between Al $K\alpha$ and Mg $K\alpha$ NaCl shake-up spectra after background subtraction (dots). Fit of the spectra (solid line) using four Lorentzian functions (A, B, C, D) convoluted with a Gaussian ($\sigma \approx 0.65$ eV due to instrumental resolution).

The peaks can be quite nicely described by Lorentzian functions convoluted with a Gaussian function with standard deviation $\sigma \approx 0.65$ eV accounting for the instrumental resolution. The Lorentzian broadening for the shake-up peaks is larger than that of the $1s$ peak by about $\Gamma_{add}$ =0.10(5) eV (half width at half maximum) indicating a sensibly lower lifetime for the double hole configuration. In Table I we summarize the relevant data concerning the four observed peaks A, B, C, D, with the $1s$ peak as a reference for the two photon sources. In particular we report the additional shake-up energies $\Delta E$ with respect to the main $1s$ peak, and the intensities in percent of the $1s$ area in the measured spectra.

While the shake-up phenomenology is well known since the early days of the photoelectron spectroscopy[4] relatively intense structures, of the order of a few percent of the main core-electron peak, have remained undiscovered for over 20 years. In particular, while the shake-up features associated with the double hole configuration $[1s2p]$ were easily observed in Ne,[5] extremely resolved peaks are now observed in solid phase systems as well opening the way to a new class of shake-up XPS experiments.

TABLE I. Observed energies and intensities for the $[1s2p]np$ shake-up peaks in NaCl and assignment.

| | Al $K\alpha$ | | Mg $K\alpha$ | | |
|---|---|---|---|---|---|
| Peak | $\Delta E$ (eV) | Int. (%) | $\Delta E$ (eV) | Int. (%) | Assign. |
| Na $1s$ | 0 | 100 | 0 | 100 | |
| A | 56.5(2) | 0.9(1) | 56.8(2) | 0.6(1) | 3pL |
| B | 61.0(2) | 1.5(1) | 61.1(2) | 1.2(1) | 3pU |
| C | 64.2(4) | 0.04(2) | 64.7(4) | 0.06(3) | ? |
| D | 68.7(4) | 0.07(2) | 69.0(4) | 0.12(3) | ? |

A certain similarity between the Ne and NaCl spectra is expected because the $Z$ numbers are very close and especially because the NaCl is a ionic compound with the ion $Na^+$ isoelectronic with Ne. In NaCl the effective potential felt by the $2p$ electron after excitation in the presence of a $1s$ hole is dominated by a strong spherically symmetric perturbation to the crystal field. The atomic $3p$ wave function is confined in a limited region of space around the excited atom so that it is reasonable to use an atomic classification scheme.[15] For higher values of the principal quantum number the atomic wave function extends considerably over neighboring sites requiring the account for solid state effects.

Similarly to what is observed in XAS experiments on Ne and third-period atoms[7–10] also these XPS spectra appear to be dominated by the hole-hole exchange interaction $G^1(1s, 2p)$ that generates the main double peaked structure A-B split by 4.4 eV. The lower binding energy peak (A) corresponds to the $[1s2p](^3P)3p\epsilon p$ terms, usually referred to as $3p$ lower (3pL),[5] while the higher peak (B) is due to the $[1s2p](^1P)3p\epsilon p$ terms [$3p$ upper (3pU)]. This pattern is rather similar to what is seen in Ne (Ref. 5) where the first two main features split by 3.4 eV have been assigned to 3pL and 3pU states, respectively. The triplet-singlet splitting increases from Ne to Na in agreement with the increase of the exchange integral $G^1(1s, 2p)$. Besides, due to the larger excitation energy required to promote the $2p$ electron to the first available resonance, the 3pL peak moves from $\Delta E$=37.35 eV in Ne to $\Delta E$=56.6 eV in NaCl. The relative $A/1s$ and $B/1s$ intensity data reported in Table I should be corrected for the effects of the different mean free path and instrumental transmission function at the two kinetic energies. The first effect results in a reduction of the apparent intensity ratio, the second in an enhancement, both more pronounced with the Mg radiation. We estimate the actual $(A+B)/1s$ intensity ratio to be about 2% at the Mg $K\alpha$ and about 2.5% at the Al $K\alpha$. This is anyway smaller than the relative intensity of the first two peaks in Ne that amounts to 6.3% of the $1s$ intensity,[5] indicating a reduction of the overlap matrix element between $2p$ and the final state wave function from Ne to Na. The comparison between the Mg and Al $K\alpha$ sources seems to indicate the presence of energy-dependent effects on the intensities of the 3pL and 3pU shake-up channels that, together with the slight variation of the $A/B$ intensity ratio, may be relevant to discuss the adiabatic-to-sudden transition regime.

The importance of correlation effects, including initial state configuration interaction, in determining the observed intensity of the Na shake-up lines has been largely emphasized in the literature.[16] The $A/B$ intensity ratio observed in Na departs from the prediction of a simple $LS$ coupling calculation more than in the Ne case, indicating an even larger importance of correlation effects in the process and stimulating further theoretical investigations.

The spectra reported in Fig. 3 present two weaker features labeled C and D that can be subject of a tentative assignment. As a first guideline, the similarity in the shake-up patterns between NaCl and Ne may suggest to

assign them to higher atomic $np$ levels like 4pL and 4pU. This assignments should be performed with extreme caution because of the presence of solid state effects. Experimentally there is no evidence for any splitting of the B peak into the two components 3pU and 4pL that might have merged into the single peak due to the increase of the $L$-$U$ splitting from Ne to Na.

Other completely different explanation for these weaker features can, however, be proposed. A careful comparison of the Al and Mg $K\alpha$ spectra from Fig. 3 as well as Table I reveals that peaks C and D are almost twice as intense with the Mg radiation. This detail provides a weak indication that they could be associated with surface effects. Indeed the kinetic energy of the photoelectron increases from about 120 eV with the Mg radiation to about 355 eV with the Al one, corresponding to a reduction of the photoelectron mean free path of a factor of about 2. The scanty available experimental evidence on peaks C and D does not allow a definite conclusion on their origin; further experiments will be required.

The success of the present experiment has been to identify a shake-up multiplet structure, clearly split by the hole-hole exchange interaction, associated with the $[1s2p]$

hole configuration in solid systems of third-period elements. The intensity of the upper and lower channels amount to about the 2% of the main $1s$ single-electron channel and appear to depend slightly on the photon energy. This phenomenology stimulates further investigations using high flux tunable photon sources. Similar experiments can be performed to detect the shake-up peaks associated with the $1s$ excitation on other third-period elements. Besides the interest in these phenomena to understand correlation effects[16] and the complex phenomenology associated with $[1s2p]$ double core-hole excitations in third period elements,[7-10] this spectroscopy might have unpredictable application to the study of condensed phases of matter containing these atoms, Si included. All these experiments will benefit from the availability of the new, third generation, synchrotron radiation sources.

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