

Double core excitations in LiI: Evidence for multicenter coupling in resonant inelastic soft x-ray scattering spectra

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Resonances in inelastic soft x-ray scattering spectra of LiI, in which final states with Li 1s as well as I 4d vacancies are populated have been observed. The intermediate states involve both Li 1s double core excitations and I $|4p^{-1}+4d^{-2}4f\rangle$ states. It is suggested that the spectra are influenced by multicenter coupling.

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I. INTRODUCTION

Core orbitals are localized at a single atomic site, and in compounds they are only a little influenced by the surroundings of the corresponding atom. Observations that seem to indicate electronic transitions between core levels at different sites have therefore always attracted attention in the community of x-ray spectroscopists.^{1,2} They challenge both spectroscopic common sense and theoretical descriptions of x-ray spectra in which the so-called one-center approximation³ is still the conventional starting point.⁴ In addition, the sensitivity to the nearest-neighbor species, bond distance, and type, which is necessarily associated with any multicenter transitions, gives them a large potential for applications in chemical analysis, especially of disordered compounds.

Such applications were also envisioned when electronic decay of highly excited states with a core hole on one atom to states with a core hole on a neighboring atom^{5,6} was observed. Influences on the angular distribution of photoelectrons associated with core excitations on neighboring atoms have also been demonstrated.⁷ For innervalence vacancies in clusters interatomic Coulombic decay,⁸ involving valence orbitals centered on the neighbors, is now well-established.

Here we show that at certain excitation energies resonant inelastic soft x-ray scattering (RIXS) populates final states with vacancies in shallow core levels *on different atomic sites*. In LiI final states with Li 1s vacancies, as well as I 4d vacancies are reached. The resonances appear in the region of the strong Li double core excitations,⁹⁻¹¹ which have been discussed for all lithium halides in Ref. 11. In LiI states associated with the highly correlated I “4p” level are also energetically allowed in this same energy region. As these “4p” states are strongly mixed with the $4d^{-2}4f$ configuration this must be seen as a second example of a RIXS mechanism involving double core hole excitations. The resonant behavior suggests that the two processes are coupled.

II. EXPERIMENT

The measurements were made at beamline I511 (Ref. 12) at MAX-lab. Radiative decay spectra were measured using a grazing incidence Rowland spectrometer¹³ measuring in the direction of polarization of the incoming radiation. The energies of the monochromator and the spectrometer were matched using the diffuse reflection of the incoming radia-

tion, and calibrated to better than 0.1 eV. Diffuse reflection also established the spectrometer function [full width at half maximum (FWHM) ≈ 0.3 eV at 89 eV]. The resolution of the monochromator was 0.05 eV at 148 eV. The photon flux was around 10^{12} photons/s delivered in a $20 \times 50 \mu\text{m}$ spot, and the data acquisition time was around 1 h per spectrum. Radiation damage in Li halides, associated with metallization, is directly reflected in the appearance of the Li metal hypersatellite¹⁴ in the signal from the studied sample. A new spot on the sample was selected every 10 s for RIXS measurements, and every 5 s for partial fluorescence yield (PFY) measurements. Under these circumstances no metal signal could be detected. In the signal from the studied sample there is a contaminating silicon L emission background,¹¹ which has been subtracted from the present data, under the assumption that its total intensity remains independent of the excitation energy within the studied range. We cannot account for the source of this contamination.

III. RESULTS AND DISCUSSION

The two-dimensional scattering map of LiI (Fig. 1) shows a sharp resonance corresponding to final states around 60 eV, when the excitation energy is tuned to 146 eV. This resonance can be assigned to localized Li 1s double excitations, populating single Li 1s core hole final states.⁹⁻¹¹ As a starting point we assume single-configuration states, and the two-step picture for the scattering event. If e_{Li} denotes an electron localized on the Li site, the resonant scattering process from the ground state (GS) to the final state can then be written

$$\text{GS} \rightarrow \text{Li } 1s^{-2}e_{\text{Li}}e_{\text{Li}} \rightarrow \text{Li } 1s^{-1}e_{\text{Li}}. \quad (1)$$

At higher excitation energies there is a diagonal line in the scattering map, starting around 148 eV excitation energy and 60 eV emission energy. This feature has maximum intensity at a constant difference in excitation and final state energies (emission energy) of around 88 eV. The dispersion reflects electron delocalization in the intermediate state. The double core hole states have one localized electron, and one electron in the conduction band, e_{CB} . This electron is a spectator during the decay which populates final states with one core hole and one electron in the conduction band:

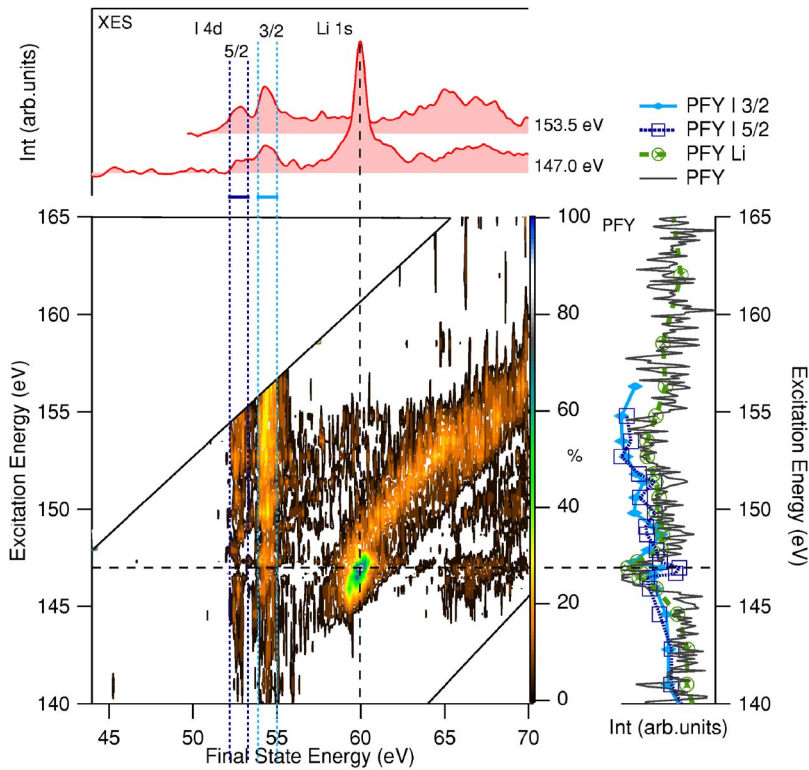
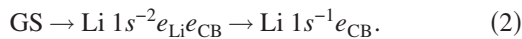


FIG. 1. (Color online) Two-dimensional scattering map of LiI, with color coded intensity as a function of excitation and final state energy. Two scattering spectra (smoothed), excited at 147 and 153.5 eV, are shown at the top of the graph, indicating structures associated with I 4d and Li 1s vacancies. PFY spectra, monitoring the 83–92 eV emission energy region are shown in the right panel. PFY is the photon yield, directly as measured, and the other spectra are constructed from the scattering map, with the labels PFY I 5/2 and 3/2 corresponding to the 52.3–53.3 and 53.9–55 eV final state energy intervals, respectively, and the PFY Li label corresponding to the 84–89.7 eV emission energy interval. For all these spectra a background determined from the spectrum excited at 137 eV, far below the relevant resonances, has been subtracted.



These two types of scattering pathways have been observed in all lithium halides.¹¹ Specific to LiI is the additional feature with two rather sharp structures with maxima at 53.0 and 54.7 eV energy loss. The energy difference, 1.7 eV, is very close to the spin-orbit splitting between $j=5/2$ and $j=3/2$ coupled pure I 4d hole states. The spectral structures are similar to features in the near-edge I 4d absorption spectrum of KI and other ionic iodine compounds,¹⁵ which have been assigned to excitations of electrons from the I 4d level to the conduction band. The assignment of the RIXS features to states with I 4d vacancies is therefore unambiguous.

We now turn our attention to the resonant scattering mechanism by which I 4d final states can be populated. The excitation energy is far below the I 4s states and deeper core levels, which therefore cannot contribute to the scattering mechanism. The energy reaches, however, the continua of the “I 4p” states.^{16–18} The quotation marks are motivated by the extremely strong correlation which leads to complete breakdown of the one-electron orbital picture. In the configuration interaction description the $4p^{-1}$ configuration strongly mixes with the $4d^{-2}4f$ configuration, resulting in a multitude of broad continuum states, spread out over around 50 eV from the first threshold, which we estimate to be around 125 eV in LiI. Energetically, these states could all contribute to the RIXS process. Designating these states $|4p^{-1}+4d^{-2}4f\rangle$, we assign the principal RIXS mechanism for population of final 4d holes to the following excitation-emission path:



Both configurations give dipole allowed intensity in the second step of the scattering process, and because of the large

orbital overlap, both $4d \rightarrow 4p$ and $4f \rightarrow 4d$ matrix elements are very large. Note, however, that this radiative transition must compete with the super-Coster-Kronig decay, the amplitude of which is normally orders of magnitude larger than the amplitude of radiative transitions, thus decreasing the *probability* for this kind of scattering pathway. Therefore we find it remarkable that this type of RIXS scattering can be observed at all.

The sharpness of the RIXS peaks ($\text{FWHM} < 1$ eV), and the constant energy loss over a large excitation energy range (at least 13 eV) (see Fig. 2) suggest that the electrons in the final states to some extent are localized at the iodine site. The splitting between the two peaks, however, suggests that the spin-orbit coupling of the d -hole is large compared to the electron-hole coupling in these states. For the near-edge absorption spectrum an interpretation in terms of local partial I p density of states close to the bottom of the conduction band in similar iodine compounds turned out to be successful,¹⁵ with a possible small excitonic shift.

The condition for observing constant-energy loss features is not necessarily localization. Using the RIXS theory of Tulkki and Åberg¹⁹ it can be shown that constant-energy loss features appear where the width of the resonances is larger than the spectral variation in the density of oscillator strength corresponding to first-step transition to an intermediate continuum state. At the $|4p^{-1}+4d^{-2}4f\rangle$ resonances we are clearly in this limit.

At higher energies above the I 4d threshold absorption spectra of iodine compounds are dominated by the strong $4d^{-1}4f$ resonance.¹⁶ In the RIXS spectra, on the other hand, there is no appreciable intensity at the corresponding energy losses. We believe that the difference can be understood in terms of the selection rules. Assuming the dipole approximation and LS coupling to be valid, only the odd 1P_1 states are

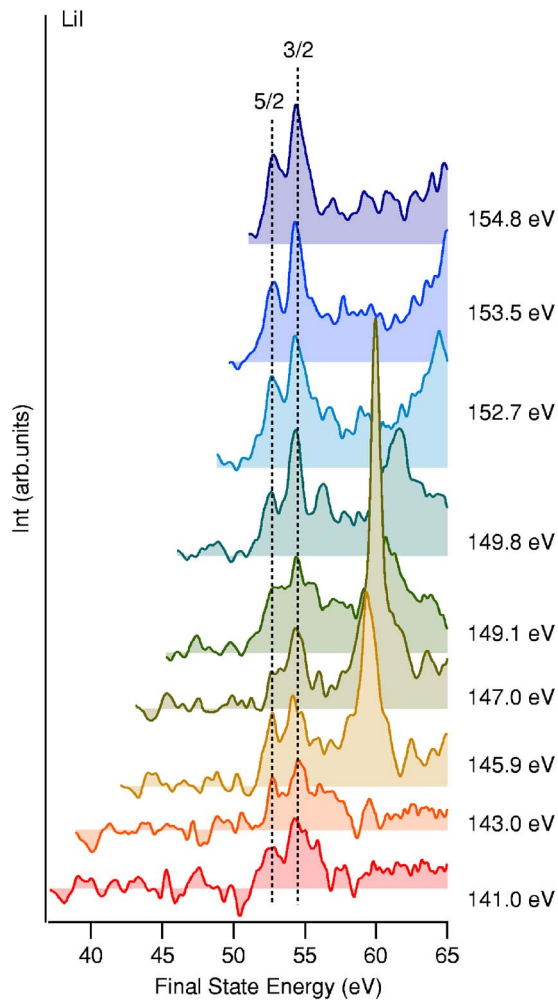


FIG. 2. (Color online) The same data as in Fig. 1, presented as a series of spectra (smoothed). Here it is obvious that the I scattering spectra change both in intensity and shape as the excitation energy is tuned in the region of the Li $1s$ double resonances.

allowed in direct absorption, and this is also the term associated with the $4d^{-1}4f$ resonance. Odd 1P_1 states are, on the other hand, forbidden in the two-photon scattering process. In the present experimental geometry the population of even 1D_2 states would be emphasized.

With this assignment the observed scattering involves intermediate states with two core holes, namely two holes in the $I4d$ shell. So far such resonances have only been observed in the solid state as Li $1s$ double excitations.^{9–11} Note, however, that the physical mechanism is very different; crudely speaking the lithium double excitations can be associated with initial state correlation, whereas the iodine double excitations primarily are due to final state correlation.

Now we turn our attention to the fact that the scattering process populating final states with an iodine core vacancy seems correlated with the population of lithium core vacancies. At excitation energies below the edge for population of Li final states there is also very little population of $I4d$ final states. The $I4d$ population increases where the Li $1s$ population has the main resonance and above the Li ionization thresholds they both have a rather excitation-energy independent cross section (Figs. 1 and 2).

This excitation-energy dependence suggests a cross-section interdependence which requires interaction between core levels on both lithium and iodide sites. To understand this coupling theoretical development is needed, and here we briefly make some general speculations. We have earlier shown^{9,10} that a double core vacancy on the lithium site in LiCl strongly polarizes the bond, so that it locally gets substantial covalent character. The iodine ion in LiI has large dipole polarizability,¹⁸ and the orbitals will strongly relax to screen a Li double excitation. As the electrons in the $I n=4$ shell show strong collective behavior, any relaxation is associated with virtual dipole excitations. It is conceivable that a multicenter coupling could be understood in terms of such excitations.

IV. CONCLUSION

We have found that RIXS excited in the region of Li double core resonances in LiI populates final states with a single Li $1s$ as well as a single $I4d$ vacancy. The results suggest a coupling between the intermediate states.

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