

Aggregation State Effects in Auger Spectroscopy: The Fluorine *KLL* Spectrum of KF

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We show by extensive Green's function calculations that the fingerprinting double peak observed in the title spectrum of the crystal is a pure nonatomic aggregation state effect, *not* to be seen in the gas phase spectrum. We clarify the mechanism for this effect as being due to the energy shift of hole-localized states induced by the crystal field and their strong mixing with close lying, otherwise Auger inactive, states. The generality of the phenomenon is discussed, identifying cases where it could be observed in the gas phase and *not* in the crystal.

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In Auger spectroscopy the study of chemical shifts, as a function of chemical environment and aggregation state, is an established tool for chemical analysis [1]. In accordance with the pronounced intra-atomic nature of Auger decay rates, environmental effects are usually observed to consist essentially of a rigid energy shift of the spectrum, possibly accompanied by detectable changes in broadening due to variations in the core hole lifetimes and nuclear dynamics (see, e.g., Refs. [1,2]). By presenting the results of extensive *ab initio* Green's function calculations of the Auger spectra of potassium fluoride, we would like to point out in this Letter a general mechanism for very strong aggregation state effects which may destroy the atomlike appearance of spectra and produce intense unexpected features.

As typical examples of atomlike behavior, the fluorine *KLL* Auger spectra of most ionic fluorides [2-6] show a distinctive and very intense first (lowest ionization energy) peak due to the dicationic states which essentially originate from the removal of two *p* electrons of a single F^- ion. Because of ionicity, the atomic character of these spectra is usually sufficiently pronounced, both in the gas phase and in crystals, for a unique peak to be observed, correlating with the 1D state of F^+ and broadened on the left by the presence of a 1S -like state. There is a remarkable exception to this situation in the spectrum of solid KF [3,6], where the first peak is split into two very evident components separated by 2.4 eV, the first of these somewhat less intense and narrower than the second. This apparent "extra peak" feature is absent in the corresponding Auger spectra of lighter alkaline and alkaline-earth fluorides [2,3,5,6]. It is also not visible in the spectrum of CaF_2 , while in the fluorides of some heavier elements of groups I and II a very weak feature can be seen, at varying relative energy from the main peak, which suggests a correlation with the double peak of KF [6]. The deviation from the atomic appearance of these spectra, especially of KF, is somewhat surprising at first, in view of the strong ionic character of the systems which would seem to be too uniform

throughout the fluoride series to account for these differences. A qualitative explanation for these observations has been proposed [6] within a fully atomic picture by invoking an electron transfer relaxation mechanism from the metal atom to the fluorine atom, which occurs after Auger decay and "is fast enough to affect the emitted Auger electrons" [6]. In practice, this relaxation process would involve the interaction among unrelaxed atomic states where two holes have been created on a fluorine site (these states carry the Auger intensity) and close lying unrelaxed states where one hole resides on each of the metal and F atoms. The interaction gives rise to final (relaxed) states which share Auger intensity, and their energy separation would account for the observed split of the Auger peak. Furthermore, the relative energy of the 3*p* electrons of potassium and the 2*p* electrons of fluorine in KF would ideally fulfill the conditions for this relaxation interaction to be strongest.

It seems rewarding to investigate quantitatively these phenomena within a correlated *ab initio* framework which permits the accurate calculation of a large number of final dicationic states, in order to analyze in more detail their real nature and the conditions for their occurrence. In particular, a point in doubt and of primary interest has so far been scarcely addressed and concerns in general the effects of the aggregation state of the sample on its Auger spectrum. As we mentioned above, one would qualitatively expect, especially in view of their atomlike character, that the only essential difference between the gas phase and solid state spectra is an approximately constant energy shift of all the peaks. The fluorine *KLL* spectrum of LiF, measured for both the solid salt and the vapor [2], provides an appropriate example of this. On the other hand, it seems clear that the appearance of any nonatomic features may be noticeably influenced by the aggregation state of the sample. The fluorine Auger spectrum of KF, with its strikingly atypical profile, appears to be a good candidate to investigate these effects and we would like to establish whether the fingerprinting double peak is a distinctive feature of

the crystal or could also be observed in the gas phase spectrum. The latter, to our knowledge, has not been experimentally measured.

Using the Green's function second order algebraic diagrammatic construction method [ADC(2)] [7], we have computed the valence double ionization spectrum of the KF molecule at its gas phase equilibrium internuclear distance (2.17 Å) [8] with a double-zeta basis set augmented with polarization functions [9]. The resulting theoretical F 1s Auger spectrum is reported in Fig. 1(a). The spectrum has been obtained from the Gaussian convolution of the computed dicationic states using a one-center estimate [10] of the Auger intensities and Gaussian components of fixed width (full width at half maximum of 2 eV). The one-center approximation to the intensities is obtained by first projecting the molecular orbitals of KF onto the F atomic orbitals obtained in the same basis set. The Coulomb matrix elements, which are combined via the Green's function two-hole (2h) spectroscopic factors to give the Auger transition amplitudes, are then expanded in atomic matrix elements for which available values [11] are used.

The spectrum shows the typical fluoride main features, with three distinct zones of intensity (between 30 and 43 eV, between 50 and 65 eV, and around 82 eV) cor-

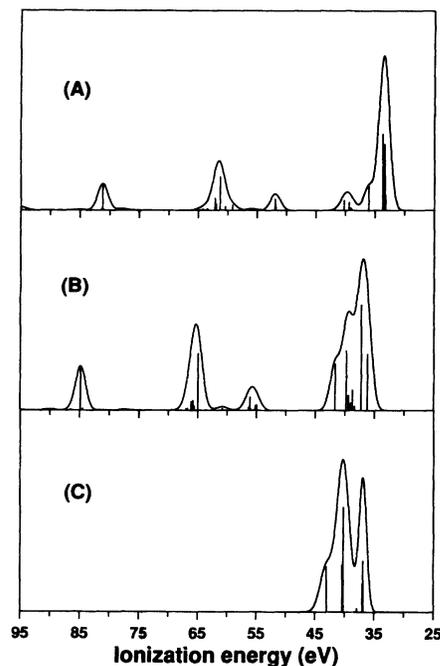


FIG. 1. Computed fluorine *KLL* Auger spectra of KF. The vertical bars show the contributing Auger transitions, with heights proportional to their computed intensities. The spectra are obtained by Gaussian convolution (see text). (a) Gas phase spectrum. (b) Spectrum of a simple point charge model of a KF chain. (c) Low energy portion of the solid state spectrum, from calculations on a K_6F^{5+} cluster embedded in a lattice of point charges.

responding essentially to the removal of $2p$, $2p-2s$, and $2s$ electron pairs, respectively, from the fluorine atom. Thus, the spectrum appears essentially atomiclike in character and, in particular, the first band peaking at 33.5 eV shows an unresolved intense 1D component composed of the $^1\Pi$, $^1\Sigma^+$, and $^1\Delta$ molecular states, and a high energy shoulder (1S) corresponding to a second $^1\Sigma^+$ state. The separation between the intense $^1\Pi$ and $^1\Delta$ states is only 0.33 eV. According to these results, the strong degeneracy lifting which would explain the split of the main peak is ruled out in the gas phase spectrum of KF and we should, therefore, look for its origin as a pure solid state effect. It can be noticed, however, that Fig. 1(a) shows an evident *nonatomic* feature, which is absent in the theoretical spectra of other alkaline and alkaline-earth fluorides (LiF , NaF , BeF_2 , MgF_2) [12,13], computed at about 40 eV and well separated from the main peak. There is no reported account of this feature in the experimental spectrum of *crystalline* KF [6]. In fact, the other prominent peaks in the computed spectrum are also accompanied by very weak nonatomic features, barely visible at ≈ 57 eV and ≈ 78 eV.

To investigate the nature of these additional features and to have a quantitative picture of the hole distribution in the final states, we can resort to a "population analysis" of the computed dicationic states [14]. Through this procedure we can separate the total charge distribution in contributions, each describing a different atomic localization situation of the two holes. We thus define a K^{-2} and a F^{-2} component describing the localization of both holes on the K and F atoms, respectively, and a $K^{-1}F^{-1}$ component, describing localization of one hole on K and one on F. The analysis, whose results are displayed in Fig. 2(a) for a few exemplary low lying states, evidences a more complex situation than the largely atomiclike ap-

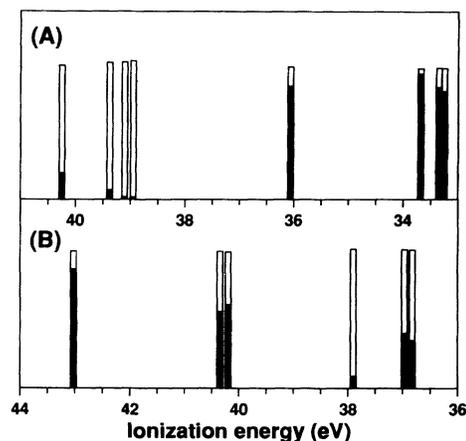


FIG. 2. Two-hole population analysis (see text) of some representative low lying dicationic states of KF. The black portion of the bars shows the F^{-2} population, the white portion the $K^{-1}F^{-1}$ population. (a) Gas phase KF molecule. (b) Solid KF.

pearance of the spectrum would suggest. The states responsible for the intense bands in the spectrum are of course dominated by the F^{-2} component. These are relatively few in number. All other states, starting already below 39 eV and up to ≈ 61 eV, have a dominating $K^{-1}F^{-1}$ character. Only at higher energy do states with significant K^{-2} weight start to appear. We thus find that the gap between the lowest (F^{-2} -dominated) states and the appearance of the $K^{-1}F^{-1}$ -type ("two-site") states is about 5 eV.

It is useful to compare this situation with that computed for other (gas phase) fluoride dications. In NaF [13] we find the first occurrence of states having significant $Na^{-1}F^{-1}$ components at about 20 eV above the lowest F^{-2} states. Because of this large energy gap, the former states have no intensity in the Auger spectrum. In polyatomic fluorides (BeF_2 , BF_3 , CF_4 , MgF_2 , SiF_4) a different localization pattern tends to prevail [13-15], due to the presence of more fluorine atoms: the central atom hardly carries any fraction of electron vacancy and the two holes are instead essentially localized either each on another fluorine atom or both on the same fluorine. From the hole population analysis of KF^{2+} we also notice that, although hole localization is generally predominant, a number of the states mainly characterized as having one hole on K and one on F exhibit a non-negligible F^{-2} component. This explains their appreciable intensity in the spectrum, in particular of the states underlying the small peak appearing at ≈ 40 eV [see Fig. 1(a)]. Of course, as mentioned above, this peak appears to be too weak and separated from the main peak to be identified with the extra peak observed in the experimental spectrum.

The above analysis of the charge distribution in the dicationic states of gaseous KF leads straightforwardly to a qualitative prediction of the changes to be expected in the Auger spectrum of the solid state, by examining the effects of the ionic crystal field on the close lying one-site F^{-2} and two-site $K^{-1}F^{-1}$ states. In the cubic ionic crystal each F^{-} ion is surrounded by six neighboring K^{+} ions. The electrostatic effect of the crystal Madelung field [16] is thus to stabilize the fluorine electrons with respect to the isolated molecule situation, which in turn implies an increase in their ionization energy. For exactly opposite reasons one should find, instead, a decrease in the ionization energy of the destabilized potassium electrons. Based on this picture, one can immediately conclude that the crystal potential should affect the double ionization energy of the F^{-2} -type states much more than it affects the $K^{-1}F^{-1}$ states. In particular, in qualitative terms, the ionization energy of the F^{-2} states should increase appreciably while that of the $K^{-1}F^{-1}$ states should not vary much. These considerations suggest a satisfactory mechanism to explain the observed Auger profile: The gap between the lowest F^{-2} states responsible for the first peak in the spectrum and the manifold of $K^{-1}F^{-1}$ states is largely reduced in the solid with respect to the 5 eV computed in the molecule, giving rise to a stronger

interaction and redistribution of intensity. In fact, this simple electrostatic model, using the Madelung lattice energy and accounting for the increased bond distance in the KF crystal (2.67 Å) [17], gives an estimated shift of the F^{-2} states relative to the two-site states of the required order of magnitude (6.8 eV). Undoubtedly, if confirmed, this appears to be an unusual and remarkably large aggregation-state effect on Auger spectra.

As a preliminary demonstration of the above picture we have repeated the Green's function calculations on the KF molecule introducing point charges to simulate a linear chain of ions. This simple model still allows us to calculate the whole Auger spectrum with no extra computational effort although incorporating qualitatively the relevant electrostatic effects. Six unit point charges of alternating sign have been placed on each side of the molecule along the KF axis, the distance between neighboring charges being equal to the internuclear distance. The resulting fluorine Auger spectrum, obtained as described above, is shown in Fig. 1(b). The effect of the charge field on the profile of the first peak is evident and confirms the plausibility of the proposed phenomenon. The groups of F^{-2} and $K^{-1}F^{-1}$ states merge in one group between 35 and 40 eV, and their interaction gives rise to a marked energy splitting and intensity redistribution due to the sharing of F^{-2} character. The spectral band shows two maxima separated by 2.3 eV. The first (lowest energy) maximum is again mainly due to a $^1\Delta$ and a $^1\Pi$ state. Several states contribute to the additional peak, in particular, a second $^1\Pi$ state which acquires roughly the same F^{-2} character as the first.

Finally, in order to provide a conclusively reliable theoretical simulation of the crystal spectrum, we have carried out a Green's function calculation on a large cluster composed of a K_6F^{5+} unit, using the same basis set as above (244 basis functions). The cluster has been embedded in a cubic lattice of 118 point charges, thus simulating a cell of 125 ions centered around a fluorine site with O_h symmetry. The point charges on the outermost layer are not unity but have instead been uniformly altered to make the whole cell neutral. Finally, the residual lattice potential at the K and F sites, in order to achieve the correct limit value of 8.3 eV [18], has been accounted for in the Green's function calculation by suitably shifting the Hartree-Fock one-electron energies, by 2 eV for the F electrons and by -0.5 eV for the K electrons. The interionic distance used is 2.67 Å [17]. Because of the large size of the cluster, we have limited our calculations to the lowest energy part of the double ionization spectrum underlying the first Auger peak.

The results of this cluster simulation yield the theoretical Auger band shown in Fig. 1(c). The doubly peaked structure of the band due to solid state aggregation appears now evident, and its overall profile reproduces the experiment quite satisfactorily. The energy separation between the two band components is somewhat overestimated by the calculations (3.3 eV), which may be mainly

ascribed to the finite size of the cluster and in particular to the lack of a true F^- coordination layer beyond the six K^+ ions. The states mainly contributing to either peak are found to be of ${}^1T_{2g}$ and 1E_g symmetry. The corresponding computed two-hole population distribution is shown in the bar plot of Fig. 2(b). By comparing with the data of the gas phase analysis of Fig. 2(a), one can immediately see the increase in double ionization energy of the former pure F^{-2} states and their mixing with the $K^{-1}F^{-1}$ states. Note that the uppermost F^{-2} state shifts from ≈ 36 eV to ≈ 43 eV, thus "overtaking" the group of $K^{-1}F^{-1}$ states and largely retaining its character. It is important to note, in addition, that the computed F^{-2} and $K^{-1}F^{-1}$ character of the states is not the same in both peaks of the solid state spectrum: the states underlying the lowest energy component retain a larger (approximately 5:3 on average) $K^{-1}F^{-1}$ hole population. This finding is also in very good accord with the experimental observations, for it explains not only the somewhat weaker intensity of the first peak, but also its relative narrowness compared to the second: The F^{-2} character is associated with a charge distribution in the final states presenting two neighboring K^+ and F^+ ions, whereas the $K^{-1}F^{-1}$ contribution corresponds to a structure in which a K^{2+} ion lies close to an approximately neutral F site. The much more repulsive local site-site interaction associated with the F^{-2} character should, therefore, be expected to cause a larger broadening of the corresponding Auger transitions due to more effective phonon excitations. This has been approximately taken into account in the spectrum of Fig. 1(c) by giving a smaller width to the states underlying the first peak than to those composing the second (1.5 eV and 2.5 eV, respectively).

In conclusion, with the aid of extensive *ab initio* Green's function calculations on both the KF molecule and on a large cluster simulating all the relevant features of the ionic crystal, we have demonstrated that the atypical double peak appearing in the fluorine *KLL* Auger spectrum of solid KF is a genuine aggregation-state effect and should *not* be observed in the gas phase spectrum. For the isolated molecule, a pronounced atomic localization of the two electron vacancies in the dicationic final states is predicted by the calculations, giving rise to the typical atomiclike fluorine spectrum where essentially only the one-site F^{-2} states contribute. In the solid phase, the F^{-2} states are shifted up in energy by the crystal field and, in the outer valence region, interact strongly with close lying $K^{-1}F^{-1}$ states. As a result, hole delocalization takes place, with a pronounced redistribution of Auger intensity causing the splitting of the fluorine band. In strongly ionic systems, such as the fluorides, this large dependence of the potential on the aggregation state is of course a general feature and always produces very different energy shifts on one-site and two-site hole localized dicationic states. When these are well separated in energy, only the former states contribute to the Auger

spectrum, which is essentially atomiclike. Their interaction may instead give rise to intense nonatomic features in the spectrum. The clarification of this mechanism for aggregation-state effects should make evident that the appearance of such environmental nonatomic features in Auger spectra of ionic systems is by no means to be expected in general only in the solid state. In fact, it is easy to envisage the opposite situation, in which hole localization is effective in the crystal phase and delocalization occurs in the vapor. In this connection, it is very interesting to note [6] that in the solid state spectra of some fluorides of heavier elements, such as RbF and CsF, the two-site states are essentially Auger inactive and appear to lie 4–7 eV *lower* in energy than the F^{-2} states: the measurement of the gas phase spectra of these systems would be highly desirable to further investigate our surmise.

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