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Auger spectrum of the LiF molecule

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The Auger spectrum of LiF vapor has been measured in the energy region 600–680 eV by means of electron-beam excitation. The assignment of the peak structure is based on theoretical *ab initio* calculations with the use of the multiconfigurational complete-active-space self-consistent-field method and by comparison with the corresponding spectra of the neon atom and the hydrogen fluoride molecule.

I. INTRODUCTION

Auger spectra of molecules with the two-hole final states involving valence orbitals are very complex. Application of electronic structure theory for the interpretation of such spectra has so far been confined to two classes of molecules—covalent diatomics and noble-gas isoelectronic hydrides (see, e.g., Refs. 1, 2, and 3). With the advent of techniques for recording Auger spectra of ionic molecules new areas for theoretical investigations have now been opened up. In this paper we will report a detailed experimental and theoretical analysis of the *KLL* Auger spectrum of the LiF molecule. This spectrum represents an interesting link between the previously well-studied HF and Ne spectra. In the theoretical energy analysis the electron correlation effects have been considered with the use of a multiconfigurational self-consistent-field (SCF) approach, known as the complete active space SCF method.

II. EXPERIMENTAL

The experimental Auger electron spectra were measured by means of a cylindrical mirror type electron spectrometer at the University of Oulu. A resistance heated high-temperature oven system was used to vaporize the LiF sample. The primary ionizations were caused by a 3-kV electron beam with typically 1 mA of beam current. No retardation of the Auger electrons was used and the observed intensity was corrected for the varying transmission of the analyzer. The spectrometer was controlled and the data was collected by a microprocessor based system. The final spectrum was obtained as the sum of several collections, adjusting the peak positions carefully before the summing. The resolution of the spectrometer corresponds to the linewidth contribution of about 0.5 eV which is a minor factor to the observed narrowest linewidth of 1.3 eV.

The energy calibration of the spectrum was done by the standard procedure, measuring the spectrum of LiF simultaneously with the spectra of Ar and Ne. The applied energies for the Ar $L_3M_{2,3}M_{2,3}(^1D_2)$ and Ne $KL_{2,3}L_{2,3}(^1D_2)$ lines were 203.50 and 804.46 eV, respectively.

In addition to the subtraction of a constant background, a smooth background shape was also subtracted from the experimental spectrum. This background was assumed to increase by each channel in going from higher to lower energies proportionally to the net intensity of this channel. Each background increment was further assumed to attenuate exponentially. The background-subtracted spectrum was further decomposed into line components by a least-squares fitting procedure. The decomposed spectrum is shown in Fig. 1. The absolute energies, relative intensities and widths of the lines obtained from the fit are given in Table I.

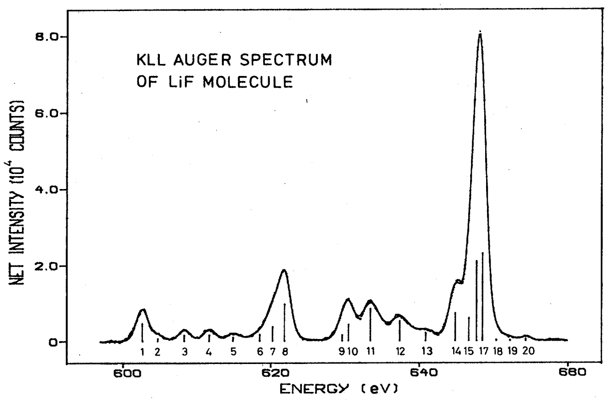

FIG. 1. Experimental *KLL* Auger spectrum of LiF molecule excited with 3-keV electrons. Solid curve and vertical lines represent a least-squares fit of Voigt functions to the experimental points.

TABLE I. Experimental energies (in eV), intensities (in %), and linewidths (in eV) of the Auger electron spectrum of LiF molecule in the energy region 600–650 eV.

Line number in Fig. 1	Energy	Intensity	Linewidth
1	602.62	1.5	1.9
2	604.74	0.8	1.9
3	608.32	1.6	1.9
4	611.75	1.6	1.9
5	614.96	1.1	1.9
6	618.55	1.8	2.9
7	620.26	3.7	1.9
8	621.85	9.1	1.9
9	629.62	1.6	1.9
10	630.46	4.3	1.9
11	633.47	8.0	2.9
12	637.41	5.0	2.9
13	640.86	2.1	2.9
14	644.82	6.9	1.9
15	646.64	5.8	1.5
16	647.66	19.5	1.5
17	648.47	21.5	1.5
18	650.34	0.5	1.5
19	652.18	0.3	1.5
20	654.31	0.6	1.5

III. COMPUTATIONAL DETAILS

The Gaussian basis sets for fluorine and lithium were taken from Dunning and Hay.[4] The $(10s,5p)$ primitive functions for fluorine were contracted to $(5s,3p)$ and augmented by two d functions with orbital exponents of 0.83 and 0.14. The $(10s,4p)$ primitive functions for lithium were contracted to $(5s,2p)$. This basis set size, being of triple zeta plus polarizing quality, has in general been found to provide sufficient flexibility to account for the large valence relaxation induced by electronic transitions between core-filled and core-hole containing states, and has been extensively tested in *ab initio* investigations of Auger spectra of covalent molecules.[1] Owing to the compact character of the doubly charged final Auger states further addition of diffuse functions will only minorly perturb the computed relative transition energies.

The complete-active-space SCF (CASSCF) method[5] was used in the present calculations. In the version employed, the orbital optimization problem of the multiconfiguration (MC) procedure was solved using the "super-CI" approach. One of the basic features of the CASSCF method is that one does not need to worry about the configurations to be included in the CI expansion of the wave function. The only "chemical" choice remaining is the division of the molecular orbitals into inactive ones which are doubly occupied in all configurations, active ones among which the electrons participating in the CI are distributed in all possible ways resulting in a complete expansion, and secondary ones which are empty in all configurations. The inactive subspace comprised the 1σ and 2σ MO's (i.e., roughly the $1s$ orbitals of fluorine and lithium). The 3σ, 4σ, 5σ, 6σ, 1π, and 2π orbitals, forming three correlating pairs, were included in the active subspace. In the core-hole states the 1σ orbital was treated separately. This choice gave an MC expansion of intermediate size, typically with somewhat over 300 configurations. The energy obtained for the $(1\sigma)^{-1}$ core-hole state is 686.2 eV above that for the neutral ground state of the LiF molecule, or -81.8204 a.u.

TABLE II. The various spectral terms arising from double ionizations from the 3σ, 4σ, and 1π valence orbitals of LiF.

LiF ground-state configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4\,{}^1\Sigma^+$	
The doubly ionized states	
$(1\pi)^{-2}$	${}^1\Delta$, ${}^3\Sigma$, ${}^1\Sigma$
$(4\sigma)^{-2}$	${}^1\Sigma$
$(3\sigma)^{-2}$	${}^1\Sigma$
$(1\pi)^{-1}(4\sigma)^{-1}$	${}^1\Pi$, ${}^3\Pi$
$(1\pi)^{-1}(3\sigma)^{-1}$	${}^1\Pi$, ${}^3\Pi$
$(4\sigma)^{-1}(3\sigma)^{-1}$	${}^1\Sigma$, ${}^3\Sigma$

Those doubly ionized states of LiF that have holes in the 3σ, 4σ, and 1π orbitals have been studied. The corresponding spectral terms are summarized in Table II. In addition, various shake-up and shake-off states have been considered. The resulting transition energies are given in Tables III and IV.

IV. DISCUSSION

A. The *KLL* transitions

The assignment of the transitions in the presently reported Auger spectrum of LiF vapor is based on theoretical *ab initio* calculations using the multiconfigurational CASSCF (complete-active-space SCF) method[5] and on comparison with the closely related spectra of the Ne atom[6] and of the HF molecule.[7]

The most prominent line of the Auger spectrum of the LiF is ascribed to the $K-(1\pi)^{-2}\,{}^1\Delta$ and $K-(4\sigma)^{-1}(1\pi)^{-1}\,{}^1\Pi$ transitions. As the 4σ molecular orbital is almost exclusively F_{2p_z} in character, with only a very small Li_{2s} participation, a one-center-expansion calculation would give an intensity relation 1:1 for the ${}^1\Delta$ and ${}^1\Pi$ transitions. Indeed, a least-squares fit of two Voigt functions with 1.5-eV linewidths to the most prominent peak of the experimental spectrum showed an intensity ratio close to 1:1. Very nearly equal intensities have also been computed for the spectrum of HF.[7(b)] In HF the energy separation of the ${}^1\Delta$ and ${}^1\Pi$ transitions is 3.4 eV. On the other hand, when approaching the Ne atom limit, the two states coalesce into the ${}^1D$ state. Thus, the Ne-like appearance of this feature in the LiF spectrum may be rationalized by invoking the rather ionic character of the chemical bond causing a rather Ne-like fluorine center in LiF. The present *ab initio* calculations confirm this assignment, the energy difference of the ${}^1\Delta$ and ${}^1\Pi$ states being only 0.47 eV. The energy separation between the two Voigt functions (components 17 and 18 in Fig. 1) is 0.8 eV. However, the decomposition of an experimental peak to individual lines is not very accurate in cases where the lines lie near to each other (separated by an amount

TABLE III. The Auger transition energies from the $(1\sigma)^{-1}\,{}^2\Sigma$ core ionized state to the various doubly ionized final states.

Assignment		Transition energy (eV) Calculated	Observed	Line	Measured rate LiF	Ne (Ref. 6)	Coefficient[a]
$(1\pi)^{-2}$	${}^3\Sigma^-$	652.04	652.18	19	0.01		0.994
$(4\sigma)^{-1}(1\pi)^{-1}$	${}^3\Pi$	651.55	650.34	18	0.02		0.995
$(1\pi)^{-2}$	${}^1\Delta$	649.16	648.47	17	1.00	2.26	0.995
$(4\sigma)^{-1}(1\pi)^{-1}$	${}^1\Pi$	648.69	647.66	16	0.91		0.994
$(1\pi)^{-2}$	${}^1\Sigma^{+\text{b}}$	648.61	646.64	15	0.27		
$(4\sigma)^{-2}$	${}^1\Sigma^{+\text{b}}$	646.45	644.82	14	0.32	0.24	
$(3\sigma)^{-1}(1\pi)^{-1}$	${}^3\Pi$	630.38	630.46	10	0.20	0.30	0.990
$(3\sigma)^{-1}(4\sigma)^{-1}$	${}^3\Sigma^+$	629.93	629.62	9	0.07		0.989
$(3\sigma)^{-1}(1\pi)^{-1}$	${}^1\Pi$	618.78	621.85	8	0.42	0.95	0.886
$(3\sigma)^{-1}(4\sigma)^{-1}$	${}^1\Sigma^+$		620.26	7	0.17		0.764
$(3\sigma)^{-2}$	${}^1\Sigma^+$	600.27	602.62	1	0.21	0.46	0.997

[a] The coefficient of the leading configuration in the CI expansion of the CASSCF method.

[b] These two states are actually strongly mixed with the CI expansions being $0.73(1\pi)^{-2}-0.67(4\sigma)^{-2}$ and $0.67(1\pi)^{-2}+0.73(4\sigma)^{-2}$, respectively. For a discussion, see text.

less than or equal to the half-width of the standard line).

Another consequence of the neonlike character of the LiF system is that the $(1\pi)^{-2}\,{}^1\Sigma^+$ and $(4\sigma)^{-2}\,{}^1\Sigma^+$ states mix strongly in the MC calculations, as indicated in Table III. Reported CI calculations[2] on HF predict a separation of 6.9 eV which in the present calculation is reduced to 2.2 eV. Auger transitions to these final states most probably correspond to the peak observed at the low-energy side of the main peak in the experimental spectrum. Best fit to the observed peak structure at the energy region 644–649 eV was found by using two Voigt functions (lines 14 and 15 in Fig. 1) separated by 1.8 eV. Line 14 corresponds to the $K-(4\sigma)^{-2}\,{}^1\Sigma^+$ transition and line 15 to the $K-(1\pi)^{-2}\,{}^1\Sigma^+$ transition

The $K-{}^3\Pi$ line on the high-energy side of the $K-{}^1\Delta$ transition is positioned very near the latter peak in the calculations of the HF molecule. The LiF spectrum is found to resemble more closely that of the neon atom even in this respect, the $K-{}^3\Pi$ transition energy being 2.4 eV above the $K-{}^1\Delta$ one. In Ne the energy separations of the ${}^3P_0$, ${}^3P_1$, and ${}^3P_2$ states from the ${}^1D_2$ state are 3.20, 3.12, and 3.20 eV, respectively.[8] This line reduces to a tail both in the experimental LiF and Ne spectra.

The transition $K-(3\sigma)^{-1}(1\pi)^{-1}\,{}^3\Pi$ is computed to lie at 630.4 or 18.8 eV relative to the ${}^1\Delta$ line in the LiF spectrum. The corresponding lines in the Auger spectrum of Ne are found at 22.2 eV (the ${}^3P_{0,1,2}$ lines). The corresponding line is also present in the spectrum of HF, positioned 30.7 eV below the ${}^1\Delta$ line according to the calculations of Faegri and Kelly.[7(b)] The strong F_{2p_z} character of the 4σ MO of LiF causes the $(3\sigma)^{-1}(4\sigma)^{-1}\,{}^3\Sigma^+$ transition to lie nearer to the ${}^3\Pi$ line in the LiF spectrum than in the HF one. A fit of two Voigt functions with 1.9-eV linewidths to the asymmetric line at 630 eV in the experimental spectrum resulted in an energy separation which deviates by a factor of 2 from the theory. Owing to the uncertainties in the linewidth and shape, this finding should not be taken too literally.

The structure at 620 eV is assigned to the $K-(3\sigma)^{-1}(1\pi)^{-1}\,{}^1\Pi$ and $K-(3\sigma)^{-1}(4\sigma)^{-1}\,{}^1\Sigma^+$ transitions. In the Ne atom the corresponding state is ${}^1P_1$, lying 32.7 eV below the ${}^1D_2$ line, as the 4σ and 1π MO's of

TABLE IV. The shake-off and shake-up Auger transition energies in cases where an electron from the 1π orbital is excited/removed during the ionization.

Transition		Energy (eV) Calculated	Observed
Shake-up transitions in the range 630–645 eV			
$(1\sigma)^{-1}(1\pi)^{-1}(2\pi)^{+1}\,{}^2\Sigma\rightarrow$	$(1\pi)^{-3}(2\pi)^{+1}\,{}^3\Sigma$	642.1	
${}^2\Sigma\rightarrow$	${}^1\Sigma$	641.37	640.8
Shake-off transitions in the range 630–645 eV			
$(1\sigma)^{-1}(1\pi)^{-1}\,{}^1\Pi\rightarrow$	$(1\pi)^{-3}\,{}^2\Pi$	637.76	637.41
${}^3\Pi\rightarrow$	${}^2\Pi$	633.87	633.47
Shake-off transitions in the range 605–620 eV			
$(1\sigma)^{-1}(1\pi)^{-1}\,{}^3\Pi\rightarrow$	$(3\sigma)^{-1}(1\pi)^{-1}\,{}^4\Sigma$	609.38	611.75
${}^1\Pi\rightarrow$	${}^2\Sigma$	606.14	608.32
${}^1\Pi\rightarrow$	${}^2\Delta$	606.01	
${}^3\Pi\rightarrow$	${}^2\Sigma$	602.25	604.74
${}^3\Pi\rightarrow$	${}^2\Delta$	602.11	

LiF correlate with the $2p$ orbitals of the Ne atom. The energy differences of the two MO's explain the slight separation of the $^1\pi$ and $^1\Sigma^+$ states and consequently the broadening and asymmetry of the line observed in the spectrum. This effect is even more pronounced in the spectrum of HF.

Finally the line at 603 eV in the LiF spectrum is ascribed to the $K-(3\sigma)^{-2}\,{}^1\Sigma^+$ transition. It is related to the $K-(2\sigma)^{-2}\,{}^1\Sigma^+$ transitions in the HF spectrum which are split into three major components[2] and to the $K-(2s)^{-2}\,{}^1S$ line in the Ne spectrum.[9]

Although the widths of the deconvoluted bands considerably exceed the lifetime broadening of the core-hole state (0.1—0.2 eV for the fluorine atom[10]), no vibrational structure can be discerned. This is an indication of dissociative initial and/or final states. Self-consistent-field investigations on fluorine containing compounds predict a dissociative character for the $F(1s)^{-1}$ potential-energy surfaces[10] which can be rationalized in neonlike resonance valence structures. This mechanism probably also contributes to the comparatively broad appearance of the bands in the present LiF spectrum. Dimer formation in the target vapor may be a further factor contributing to the large observed linewidth.

In all, we find that the CASSCF calculation overestimates by roughly 2 eV the energies of the $(2p)^{-2}$ outer-outer valence band transitions while inner valence $2s$ based transitions generally are in better accord. This trend is also commonly observed for covalent diatomics when these are analyzed by means of SCF, or limited or intermediate CI calculations with wave functions encompassing the structure dependent correlation energy that emerges from internal and semi-internal (internal-external) electron excitations. The structure dependency is considerably smaller for LiF and probably also for other ionic compounds than for unsaturated covalent species. It is conveniently taken care of by the complete active space expansion of the CASSCF method, as the orbitals for each state are optimized in the "presence" of the correlated potential. Starting out from main double-hole reference configuration states, such excitations will produce important configuration state functions (CSF:s) with many open shells (high-order particle-hole expansions) making *a priori* selection schemes difficult to design. On the other hand, the resulting CAS set of CSF:s leave out a large part of the dynamical correlation energy which is represented in the wave-function picture by external excitations to higher levels, unoccupied in the ground state. The $(2p)^{-2}$ based transitions are thus consistently overestimated because the dynamical correlation of the two $2p$ electrons is partly neglected in the initial state while these electrons are missing in the final residual Auger states. This error could most probably be accounted for by means of a large-scale configuration interaction calculation on top of the CASSCF. For LiF there is little reason to anticipate that it would change the qualitative findings at the CASSCF level of approximation.

The correlation error is somewhat larger than apparent from Table III since this error is counteracted by a relativistic correction for the additional $1s$ electron in the final state. The relativistic contribution to the Auger transition energies has been estimated by Kelly to amount to 1 eV in neon[11] which, by virtue of the Z^4 rule of thumb, forms an upper limit for the corresponding contribution in LiF.

The electron correlation effect in the Auger spectrum could be anticipated to be larger in LiF than in neon because of the lowering of symmetry. On the other hand, when comparing with HF, the fact that the 4σ orbital in LiF is almost fully localized to F (whereas the 3σ orbital in HF is mainly of hydrogen $1s$ character) would suggest a more neonlike appearance with respect to the correlation effects. We find that our results favor the latter notion. Not having performed a comparative separate open-shell RHF calculation we base this contention on the appearance of the CASSCF wave functions (see Table III). For $2s$ based transitions in LiF there is a one-to-one correspondence between (spin-coupled) configurations and bands in the spectrum whereas for HF there is a splitting of configurations into many states (breakdown of the MO model), especially for the $(2s)^{-2}$ configuration which contributes with equal amounts to three different states.[2] Also, in the outermost $(2p)^{-2}$ based bands the coefficient of the leading configuration is considerably less modulated from unity in LiF than in HF or, actually, even less than in neon when comparing with the CI calculations by Kvalheim and Faegri.[2] Note, however, that this is a purely qualitative comparison since in the CASSCF approach a strong electron correlation can manifest itself in a modulation of the orbitals, as well. Such a modulation would also imply orbital nonorthogonality leading to complex considerations in an amplitude analysis.

B. The shake-up and shake-off transitions

The core ionization may be accompanied with excitation or removal of a valence electron. This leads to *KLL* shake-up and *KL-LLL* shake-off processes. Decay from such states has been detected in the Auger spectrum of neon atom and analyzed by Körber and Mehlhorn.[6]

The structure in the energy ranges 633—640 eV and 608—610 eV arises from shake-up and shake-off processes similar to the main $K-{}^1\Delta$ and $K-{}^1\Pi$ transitions but now with one of the 1π electrons excited or removed during the initial core ionization. An assignment of the observed lines is suggested in Table IV. Rather broad lines (linewidths 1.9—2.9 eV) emerge in the fit to the experimental spectrum for most of the transitions now interpreted as shake-up or shake-off transitions.

Owing to the very low-fluorescence yield ($\sim 10^{-4}$) the integrated Auger satellite intensities directly reflect the total shake-up and shake-off probability per core ionization event. This quantity is very sensitive to electron correlation in both initial and final states. It amounts to 26% for neon.[3] From a corresponding integration of the satellite intensities in the present spectrum one obtains a value of 25% for LiF. Thus, also with respect to the dynamics of direct core ionization a close resemblance of LiF with neon is warranted. Furthermore, the assignments in Table IV show that the integrated intensity of transitions emanating from the $(1\sigma)^{-1}(1\pi)^{-1}\,{}^3\Pi$ and $^1\Pi$ shake-off states relates as 1.6, i.e., the two multiplets are nonstatistically populated. This rather remarkable result has previously only been observed for neon. A value of 1.36 has been given by Auger[3,12] and an indirect (semiempirical) value of 1.8 by x-ray emission.[13] This is probably caused by continuum coupling of the two shake-off channels according to Chattarji *et al.*[14] We stress the tentative nature of our result; we assume here that there is a quasidegeneracy for 4σ and 1π shake off and we have also neglected the underlying contributions from higher shake-up states and from the $1\sigma3\sigma$ shake off. Judging from the neon Auger spectrum the probability of the latter shake-off configuration is less than 10% of that for the $1\sigma1\pi$ configuration.[3]

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