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Experimental and Theoretical Investigation of the Li 1s Spectra of Molecular Lithium Halides

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Experimental and Theoretical Investigation of the Li 1s Spectra of Molecular Lithium Halides

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The Li 1s absorption spectra of molecular LiF and LiCl have been studied for the first time by experimental as well as by theoretical methods. The strong absorption bands at the onset of the Li 1s excitations can qualitatively be interpreted in terms of a simple ionic model. The spectra are analyzed and assigned in more detail on the basis of SCF and CI calculations, and also within the framework of the Z+1 core analogy model. The limitations of this model are discussed. Li 1s ionization potentials of LiF, Li_2F_2, LiCl, and Li_2Cl_2 are derived.

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1. Introduction

The electronic structure and molecular properties of the ground state of the gaseous Li-halides have been well studied, both experimentally[1] and theoretically[2]. In contrast to this not much is known about the excited states. Only recently reliable calculations on valence excited states of LiF have been published[3,4].Optical investigations have been limited to excitations of valence electrons for photon energies below 12 eV[5-8]. Only broad absorption bands due to transitions to antibonding states could be detected in this spectral range. Detailed information on the occupied valence orbitals has been obtained from the HeI photoelectron spectra[9,10].

A maximum at 62 eV detected in the electron energy loss spectra by Geiger and Pfeiffer[11] is the only existing evidence for the excitation of inner shells of the molecular Li-halides. The technical difficulties arising from the high temperature necessary for evaporation of the Li-halides on the one hand and the vacuum restrictions in the VUV region on the other hand are the obvious explanation for the lack of experimental data.

The situation is completely different for the crystalline Li-halides for which numerous experimental and theoretical data exist[12-14]. It is well established by now that the Li 1s spectra of crystalline Li-halides are strongly influenced by local effects. Therefore the comparisons of the Li 1s transitions in crystalline and molecular Li-halides may help to shed light on the nature of these transitions and the character of the final states involved.

The ionic character of the bond and the simple structure of the Li-halides render the core excitation spectra interpretable within the framework of simple model concepts. Furthermore because of the small electron number

LiCl, and especially LiF are accessible to detailed theoretical calculations. Thus the investigation of the Li 1s spectra of LiF and LiCl can serve as a critical test for simple and more advanced theoretical models.

The experimental set up is described in chapter 2. In section 3 the experimental results are presented. A discussion of the spectra in terms of an ionic model follows in section 4. In this section we also compare the molecular spectra to the corresponding spectra of the crystalline Li-halides. Ab initio calculations of the Li 1s ionization potentials are presented in section 5. In section 6 the Z+1 analogy model is discussed. In section 7 the spectra are analyzed in terms of the analogous ionic core virtual orbital model. The vibrational structure is discussed in section 8.

2. Experimental Procedure

An outline of the experimental arrangement is presented in Fig. 1. The 7.5 GeV electron synchrotron DESY served an intense continuum source[15]. A cylindrical mirror focussed the light, transmitted through the vapour, onto the entrance slit of a 2m grazing incidence Rowland type spectrograph (McPherson Model 247). The spectra were recorded on photographic plates (Kodak SWR) bent along the Rowland circle. Since photographic plates integrate the intensity over the time of exposure, the influence of fluctuations of the intensity due to current instabilities in the accelerator, or due to small variations of the vapour pressure could be greatly reduced. The energy resolution achieved at the Li K edge with a 600 lines/mm grating and 10 μ slit width was better than 40 meV. The spectrograph was calibrated with the help of the known energy positions of the $L_{2,3}$ edges of Mg and Al[16] and the absorption lines of atomic rare gases[17,18]. The exposure times varied between several minutes and several hours.

The Li-halide vapour column was maintained inside a resistance heated tubular furnace mounted in front of the spectrograph. The temperatures ranged from 700° to 1100° C, corresponding to vapour pressures between 0.1 to 3 Torr. The length of the vapour column was 40 cm to 60 cm. Windows consisting of thin films of Carbon and Aluminum separated the vapour region from the high vacuum of the beam pipe and the spectrograph. A buffer gas of He, Ar or Kr prevented the LiF (LiCl) molecules from reaching the windows. In combination with the buffer gas the windows also served as filters suppressing higher order background. Volatile impurities were carried away by a steady flow of buffer gas. With a filling of $\sim$500 g a stable pressure could be maintained for several hours without clogging of the light path or noticeable contamination of the windows.

3. Experimental Results

Figure 2 shows the absorption spectra of molecular LiF and LiCl in the energy range from 55 eV to 68 eV. No attempts have been made to establish absolute absorption cross sections, because of the following reasons: i) there are no reliable data on the vapour pressure of the Li-halides in the temperature range covered by our measurements. Only tentative values could be obtained by the extrapolation of available data[19]. ii) the lack of reliable data prevents an exact determination of the ratio of monomers to dimers under the conditions of the present experiment. It is known that the vapour of Li-halides contains up to 50 % dimer molecules[20].

Three approximately 1 eV wide absorption bands A,B,C at 57 eV, 59.4 eV and 60.7 eV for LiF and at 57.7 eV, 59.5 eV and 61 eV for LiCl dominate the spectra at the onset of the Li 1s transitions. Two bands, D, E superimposed on a high continuous background follow at 62.6 eV and 63.7 eV for LiF and at 63 eV and 64 eV for LiCl. The band A, the high energy part of band B and the bands D and E show a weak but clearly resolved fine structure. No fine structure could be detected on the low energy side of band B and on the band C. Going from LiF to LiCl the structures get sharper and corresponding peaks shift towards higher energies. The energy positions of all maxima detected in the spectra are listed in Table I.

4. Interpretation of the spectra in terms of the ionic model

4.1 Separation of the contributions due to monomers and dimers

Due to the high concentration of dimers we expect a considerable overlap of the spectra of monomers and dimers. The analysis of the vibrational structure offers a simple way to discriminate between both contributions. The spacing of the vibrational levels of the monomers in their ground state is ∿0.1 eV which is of the same order as the energy splitting of the fine structure superimposed on the bands A,B,D and E. In contrast to this there are 6 different normal modes of the dimers with vibrational quanta between ∿0.1 eV and less than 0.01 eV[21]. Therefore a complex vibrational structure is to be expected. The overlap of hot bands which, due to the lower vibrational frequencies, play a dominant role at the elevated temperatures of the present experiment, will lead to a further complication. In combination with the limited energy resolution of the spectrograph this results in a complete blurring of any vibrational structure. However, at the temperatures used in our experiments at least two thirds of the monomers are in their lowest vibrational state. Thus a significant overlap of hot bands is unlikely. Furthermore transitions to repulsive states of the monomers will not come into play below the onset of the Rydberg transitions (∿63 eV). Therefore it seems reasonable to assign the bands A,D, E and the structured high energy part of band B to the monomers and the low energy part of band B, band C and tentatively the shoulder on the low energy side of band D to the dimers.

4.2 Interpretation of the electronic transitions

The absorption bands observed between 55 eV and 65 eV of LiF and LiCl vapour are due to one electron transitions from the Li 1s shell. The Li-halides are polar molecules. SCF-LCAO-MO calculations for the ground state clearly demonstrate the ionic character[2]. The core electrons are well described by the orbitals of the free ions. The valence orbitals closely resemble the outer halogen p-orbitals with only a small admixture of outer alkali orbitals. Therefore an interpretation of the spectra at the onset of the Li 1s absorption in terms of the corresponding transitions of the free Li^+ ions suggests itself. The fact that one electron transitions from the localized Li 1s level mainly probe that part of the final orbital close to the nucleus supports this approach.

In the framework of this "ionic model" we assign the band A and the high energy part of band B to the transition $Li^+ 1s^2 \rightarrow Li^+ 1s2p$ which is split into a σ and a π component by the molecular field. The intensity ratio of the two bands suggests the assignment of the low energy component to σ. This is borne out by ab initio calculations discussed lateron. The same transitions in Li_2F_2 and Li_2Cl_2 are assumend to be responsible for the low energy part of band B and for peak C.

The next strongly allowed transitions are those corresponding to $Li^+ 1s^2 \rightarrow Li^+ 1s3p$. Therefore we assign them to bands D and E. Inserting the energies of bands A and D and B and E respectively into the Rydberg formula we estimated the Li1s ionization limits in LiF (65.6±0.5 eV) and LiCl (65.9±0.5 eV). The corresponding p_π quantum defect of about 0.4 is typical for p type Rydberg MO's in first row molecules. In contrast the p_σ quantum defect of about 0.8 is rather large, especially for Li, and indicates strong admixture of penetrating s-type orbitals.

4.3 Comparison with the solid halides

In Fig. 2 our interpretation of the molecular spectra is indicated. For comparison the Li 1s spectra of crystalline LiF[22] and LiCl[23] are shown. Our findings support the interpretation of the solid spectra, which ascribes the strong absorption band B to excitonic excitations of the Li 1s electron to final one electron states mainly originating from 2p orbitals of the Li ion[12,14,24]. Going from LiF (LiCl) to Li_2F_2 (Li_2Cl_2) and to crystalline LiF (LiCl), the $Li^+1s^2 \to Li^+1s2p$ transitions systematically shift towards higher energies. In the solid Li-halides the maxima at the onset of the Li 1s transitions coalesce into one peak, because the Li 2p level is split in the molecules but unsplit in the cubic symmetry of the crystal. The energies of the maxima in crystalline LiF and LiCl are close to the position of the absorption line of the free Li^+ ion at 62.22 eV. This indicates the lowest excited state of Li^+ is least disturbed in the solid Li-halides.

Photoemission measurements place the bottom of the conduction band at 63.4 eV for LiF[14] and 62.3 eV for LiCl[12]. Neglecting the probably rather small electron affinities these values can serve as an estimate for the ionization potential in the solids. There is a systematic decrease of the I P from the monomers to the dimers and to the solids.

5. Ab initio calculations of vertical Li 1s Ionization Potentials

For a more detailed interpretation of the spectra it is desirable to have more reliable Li 1s IP's for the different molecular species. The experimental spectrum allowed their determination by Rydberg extrapolation only for the monomers. Furthermore these estimates are very crude as the first n=2 members of the Rydberg series are considerably disturbed because of their valence character.

Therefore we performed ab initio calculations on LiF and Li_2F_2. The gaussian lobe basis sets of Whitten[25] were chosen. 1.) For the dimer Li_2F_2 the following contractions were used: Li s (3,2,2,2,1)p(3); F s (3,4,2,1)p(5) (small basis, 30 contractions). The Li 1s orbital was represented by 3 contractions in order to have enough flexibility to describe the Li $1s^2$ and Li 1s shells. 2.) For the monomer LiF the 2p orbitals are split into two contractions. A third F 2p set was added to describe the rather diffuse F^- ion in the molecule. This basis was further augmented by an sp set of bond functions to take account of polarization effects (medium size basis, 28 contractions).

The strong interaction of the Li 1s and F 2s orbitals in the molecular ions with a core hole caused convergence difficulties with the ordinary SCF routine. Therefore single configuration wave functions have been calculated with our MC method[26], which is based on the generalized Brillouin theorem. This method guarantees that the calculated wave function is orthogonal to the lower lying singly ionized states and also avoids difficulties concerning convergence and the handling of Lagrangian multipliers.

At the calculated ground state equilibrium distance of LiF (1.56 Å), which is identical with the experimental one[1], the energy difference between LiF and $(\mathrm{Li(1s)F})^+$ in the single configuration approximation is 64.45 eV. This value differs from the true vertical ionization potential mainly by the $1s^2$ correlation energy of Li^+, which amounts to 1.18 eV. The theoretical IP of LiF (65.63 eV) obtained by adding this correlation energy to the IP given above is assumed to be accurate within about 0.1 eV.

The geometrical data for Li_2F_2 given in the literature scatter considerably[2,21,27,28]. We used R_{LiLi}=2.2 Å, R_{FF}=2.6 Å, corresponding to R_{LiF}=1.70 Å. Single configuration calculations for Li_2F_2 and $(Li_2F_2)^+$ (30 contractions) with symmetry adapted orbitals (D_{2h}) resulted in an IP of 66.07 eV. However, in a system with two equivalent nuclei strong extra correlation between the core hole and the valence shell occurs. Molecular states of this type resemble Frenkel excitons in solids and may be approximated by localizing the core hole on one of the equivalent nuclei. Of course localized orbitals in a single configuration wave function destroy the correct symmetry of the total wavefunction. In the comparable case of core excited Li_2 the symmetry relaxed SCF function and the corresponding symmetrized MC function yield nearly the same energy[29] ($\delta \sim 0.01$ eV). We assume that this will also hold for Li_2F_2. The IP of 63.68 eV obtained with a symmetry relaxed SCF function, gives a core hole - valence shell correlation (polarization) effect of 2.39 eV. For the determination of the chemical shift this IP should be compared to the 64.85 eV obtained for the IP of LiF with a similar basis (15 contractions). This IP is 0.4 eV larger than the more accurate value given above. Adding the chemical shift of -1.17 eV, thus obtained, to the correlation corrected IP of LiF (65.63 eV) yields 64.46 eV for the IP of dimer Li_2F_2. It is evident that this IP is less reliable than the IP determined for LiF. For example the IP critically depends on the geometry of Li_2F_2 ($dIP/dR_{LiF} \approx 2$ eV/Å), which is not known very accurately. It is interesting to note that the difference of the Li 1s SCF orbital energies (1.15 eV[30]) in LiF and Li_2F_2 agrees nicely with our difference (1.17 eV) deduced from the total SCF energies. Furthermore our Li 1s chemical shift can almost exactly be reproduced by the simple ionic point charge model, where only the Coulomb interaction of the one or two F^- ions with the Li^+ $1s^2$ and Li^{2+} 1s ions is taken into account. The ionization potential of Li_2F_2 is smaller than that of LiF, because of the stronger stabilization of the positive hole in Li_2F_2 by the two F^- ions. In LiF^+ this Coulomb stabilization amounts to 9.2 eV, compared to the exact stabilization of 10 eV =

$IP(Li^+)-IP(Li^+F^-)$.

According to the ionic point charge model the larger bond length in LiCl leads to a reduction of the stabilization energy by 2.1 eV. A more reliable estimate of this shift is given by the difference (1.1 eV) of the Li 1s SCF orbital energies of LiF and LiCl. Both values exceed the difference of the Rydberg limits determined experimentally (0.3 eV). In the next section the 0.3 eV will be shown to be accurate within 0.1 eV by a comparison of the calculated and experimental spectra. Finally, the point charge model predicts 0.75 eV for the IP difference between LiCl and Li_2Cl_2, whereas the most reliable value is 0.4 - 0.5 eV as will be shown below.

6. The Z+1 Core Analogy Applied to the Li 1s Spectrum of LiF

A very useful model for the interpretation of core electron excitation phenomena in atoms and molecules is the (Z+1)-analogy model[31-36]. If a deep lying core electron is excited from the vicinity of a nucleus Z into an unoccupied valence orbital, the shielding of the nuclear charge is thereby reduced by about 1 unit and the number of valence electrons is increased by one. Therefore we expect that the molecular states obtained by excitation of an electron from the core around nucleus Z will be similar to normal states of a molecule with atom (Z+1) instead of atom Z. Term values of analogous states (that is their distance from the corresponding ionization potential) of a Z+1 and a Z^* molecule will be quite similar. (In the following core excitation will be denoted by an asterisk.)

The Z+1 analog of Li^*F is BeF. From the IP of BeF (9.1 eV[37-39]) and the UV-spectroscopic energy levels[40] we obtain the term values given in the first column of Table 2. In the last column the term values of Li^*F are presented as derived from the results of the preceding sections. At first sight the agreement is not good. However, two points have to be taken into account when the core analogy model is applied.[35,36]

6.1 Geometry correction

The similarity between (Z+1) and Z^* will only hold if we compare the states of the Z^*- and (Z+1)-molecules for the same geometry. But the Z^* states are created mainly by vertical excitation from the ground state of the Z-molecules, which in most cases will differ in geometry from the ground state of the (Z+1)-molecules, because in the (Z+1)-molecule we have one valence electron more than in the Z-molecule. However, if we discuss higher excited states, that is states where the electron is excited into a nonbinding and diffuse Rydberg orbital, such complications will usually not occur, as the geometries of the Z-molecule in its ground state, and of the (Z+1)- and of the Z^*-molecules in Rydberg states differ only by a few per cent in most cases. An exception from this rule will arise if the radius of the Z, Z^*, and Z+1 cores are very different. A significant change of the core radius is expected only for elements from the upper left corner of the periodic system. E.g. the ionic radii of Li^+ and Be^{++} are 0.68 Å and 0.35 Å respectively. Therefore all analogous states of BeF and Li^*F, even the Rydberg states, will differ in equilibrium geometry.

The bond lengths of LiF have been calculated within the single configuration approximation (medium basis), except for the lowest excited $^1\Sigma$ state. In this case the orthogonality on the $^1\Sigma$ ground state was enforced by using two configuration wavefunctions. Table 3 presents the theoretical bond lengths for LiF together with the experimental values for BeF. The extra valence electron changes the geometry by 0.06 Å at maximum, whereas the different size of the metal ions changes the bond length by nearly 0.2 Å. Using the experimental spectroscopic constants[40] the vertical term values of BeF (column 3 of Table 2) have been determined at the equlibrium bond length of LiF (1.56 Å). For the n=2 states these values considerably deviate from those of Li^*F. The $\sigma^*-\pi^*$ energy gap, which is 4.1 eV in BeF at R = 1.36 Å, has only slightly decreased to 3.9 eV, whereas in Li^*F it is 2.5 eV.

6.2 Exchange correction

A second difference between the Z^* and (Z+1) systems is caused by the exchange interaction[41] between the electrons in the valence shell and the core shell, which is closed in the (Z+1) molecule, but has a hole in the core excited Z^* molecule.[35,36] The exchange interaction of the upper unpaired electron is -K for the doublet states of the Z+1 molecular radical, but K and -K for the singlet and triplet core excited states of the Z molecule. Here K is the exchange integral between the core hole and the excited electron. Therefore the core excited triplet states should be closer to the states of the Z+1 molecule than the singlet states excited experimentally. The singlet-triplet splitting is expected to be large, if the orbital of the optical electron strongly penetrates into the core. This will be the case for shallow core orbitals and for valence orbitals, which are highly localized on the core excited atom (to be met frequently in polar molecules). Therefore this effect should be large in the Li-halides. The corresponding singlet-triplet splittings have been calculated for the Li^*F states. For the strongly penetrating σ^* orbital we obtain (Li $1s\rightarrow\sigma^*$) $^1\Sigma-{}^3\Sigma$ = 0.87 eV, but for π^* only (Li $1s\rightarrow\pi^*$) $^1\Pi-{}^3\Pi$ = 0.38 eV. For the penetrating lowest 3s Rydberg orbital the correction is still 0.15 eV. It decreases rapidly for higher orbitals. Adding these corrections to column 3 of Table 2 we obtain the numbers in column 5, which agree reasonably well with the experimental term values of Li^*F, except for the Π^* state. The theoretical value is still too low by about 1 eV. The same discrepancy occurs for LiCl. The experimental $\sigma^*-\pi^*$ splitting in BeCl is 3.47 eV.[42] Correction for exchange gives 3.0 eV compared to the Li^*Cl value of 1.9 eV.

6.3 Discussion of the deviation from the Z+1 analogy model

In order to justify that the deviation is not due to a misinterpretation of the experimental spectrum we compare the experimental term values with values (column 7 of Table 2) obtained by single configuration calculations with the medium basis set. This approximation is expected to be reasonable for an optical electron outside a closed valence shell. Since the polarization of the rather soft valence shell by the optical electron is neglected, the calculated term values are both too low. However, the theoretical $\sigma^*-\pi^*$ splitting agrees with the experimental Li^*F value. The theoretical SCF term values of BeF (column 2 of Table 2) also support the assignment given above.

To test, whether correlation energy contributions might change this picture, a series of small MC calculations have been performed. We are only interested in those correlation effects present in the molecule but not in the free alkali and halogen ions. These effects may be described by excitations from the F 2p to the Li n=2 shell. All these correlation effects turn out to be small (less than 0.3 eV in both cases) and show no significant changes with bond length.

We are convinced that there is a true discrepancy in the Z+1 analogy model when applied to LiF and LiCl and that it is due to an atomic effect. According to the ionic model, the discrepancy in the molecular spectra should also show up in the spectra of the free metal ions. Indeed the 2s-2p energy difference in Be^+ (3.9 eV) is very close to the $\sigma^*-\pi^*$ difference in BeF. Correcting for the exchange effect we get 3.16 eV, comparable to the Δ value in column 5 of Table 2. Again the Li^* value is much smaller: $1s2p\ ^1P - 1s2s\ ^1S = 1.46$ eV.

So far the Z+1 analogy worked within 0.2 eV for several atoms and di- and polyatomic molecules.[31-35] Therefore this failure is somewhat unexpected and needs an explanation. The condition for the applicability of the exchange corrected Z+1 analogy model is, that the orbitals of the Z^* and Z+1 systems are very similar. This is usually the case, at least for the valence orbitals. If we represent the core orbital by a single Slater orbital the ratio of effective nuclear charges or orbital exponents of the Z^* to Z+1 system is about $Z_{eff}/(Z_{eff}+0.7)$, according to Slater's rules. This ratio is only slightly smaller than unity for all core shells of all atoms except for the K shell of the lightest elements with small Z_{eff}. For Li 1s the ratio is 0.81, which reflects the considerably different spatial extension of the Li and Be cores. For C 1s the ratio rises to 0.90 and is larger for all heavier atoms. This even holds for the other alkali atoms.

7. Trends in the spectra discussed within the analogous ionic core virtual orbital model

It has recently been shown[34,36] that the term values of core excited states are approximately given by the virtual orbital energies ε of the positive ion of the Z+1 analogous molecule. (BeF^+ for Li^*F). For the calculation of the ε's of BeF^+, $BeCl^+$ and $BeLiF_2{}^+$ the medium size basis was augmented by one sp set of diffuse orbitals on each atom and by two very diffuse s ($\xi = 0.006, 0.002$) and three p orbitals ($\xi = 0.005$) on the Be atom (large basis). The basis functions for Cl were taken from Roos and Siegbahn[43], using the following contractions: s(6,4*1) p(4,1,1). The applicability of the model is borne out by the ε-values of BeF^+ given in column 4 of Table 2 and especially by the exchange corrected ε-values in column 6. Again only the π^* value deviates significantly.

At this point a comment on the nonoccupied valence orbitals is in order. On the basis of the ionic model one would expect a Li 2sσ, as Li 2pσ , and a Li 2pπ orbital. On the basis of the LCAO model again two empty σ and one π orbital are predicted in the valence shell of LiF. However, it is known that the highest valence shell orbital especially in first row molecules is situated at rather high energies, often in the continuum. Indeed, our calculations yield only one σ^* orbital below the Rydberg orbitals, which is approximately described as Li 2s with strong Li 2p admixture ($\sigma^* \approx 0.85$ Li 2s − 0.5 Li 2p). There is a corresponding perturbation of the 3s and 3pσ orbitals.

To illustrate the trends expected in the spectra, when we go from LiF to Li_2F_2 or LiCl, we have drawn a virtual orbital energy diagram in Fig. 3. The ε values of the π orbitals are nearly identical in BeF^+ and $BeCl^+$, whereas the $\varepsilon(\sigma)$ values are raised in $BeCl^+$, because the Li ns and Li npσ orbitals are subject to a stronger repulsion by the larger Cl^- ion than by the smaller F^- ion. The calculated shifts are quantitatively confirmed by the spectra. The LiCl Π states (bands B,E) lie ∿0.25 eV higher than in LiF, the σ-bands A and D of LiF and LiCl differ by 0.8 and 0.5 eV, respectively. This implies that the IP of LiCl is 0.25±0.05 eV larger than that of LiF.

This IP results in a σ^* term value of 8.1 eV for LiCl. This value is expected to be slightly smaller than the IP of BeCl. In the literature different values are reported for this quantity: 9.5±0.5 eV[44]; 9.0[44]; 11.2 eV[38]. The latter value does not seem very reliable.

If we go from LiF to its dimer only one additional virtual orbital is obtained, designated by $2\tilde{s}$ a_1 in Fig. 3. It originates from a Li 2s orbital on the second Li atom, if the core hole is assumed to be created on the first Li atom. Because of overlap reasons the Li $1s \rightarrow 2\tilde{s}$ transition has not enough oscillator strength to be detectable. All term values of $Li^{*}F$ are shifted upwards on dimerization, because the optical orbitals now interact with two halide ions. Again the in-plane orbitals are shifted more strongly than the out of plane b_2 ones. The theoretical findings qualitatively agree with the spectrum and are consistent with the theoretical IP of Li_2F_2. On these grounds we deduce a value of 65.4±0.2 eV for the IP of Li_2Cl_2.

8. Vibrational Structure

As has already been pointed out in Sec. 4.1, the vibrational structure of the absorption bands of the monomers mainly originates from $0 \rightarrow n$ vibrational excitations. The spacings are therefore attributed to the vibrational quanta in the excited states. They are given in the last column of Table 3. They are larger than the ground state quanta, consistent with the theoretical results for $Li^{*}F$. The ionic model gives a simple explanation: the ionic attraction in $Li^{+}F^{-}$ is weaker than in $(Li^{*2+}F^{-})+e$, where the excited electron is less localized on the Li atom than before excitation. According to Badger's rule, a higher force constant corresponds to a smaller bond length. This is again consistent with the ionic model and with the ab initio results (Table 3).

9. Summary

The Li 1s spectra of LiF and LiCl in the gas phase have been recorded; vibrational structure has been resolved. The spectra consist of two strongly overlaid peak series, one from the monomer, the other from the dimer molecule. The measured peaks have been assigned and the Li 1s ionization limits (Table 4) of the four species are derived by a combination of experimental and theoretical results with an accuracy of 0.1 to 0.2 eV. Many details of the spectra are qualitatively understood within the simple ionic model, in which the spectrum of the halides is treated as a spectrum of Li^+ perturbed by the negative charge of the halide. However, it is not foreseen by this model, that only one empty σ orbital from the L shell of Li^+ exists in the halides. Ab initio calculations show that this orbital has a main contribution of Li 2s, but that it is nevertheless optically accessable from Li 1s because of strong Li 2p admixture. Semiquantitative information on the spectra is obtained from the Analogous Ionic Core Virtual Orbital Model, which nicely reproduces the differences in the spectra of the four species.

Another model, the Z+1 core analogy, which has in the recent past proven very useful in the interpretation of core excitation spectra, was not fully successful in the case at hand. After correcting for different exchange energy and for different geometry (caused by an extra valence electron in the ground state of the Z+1 molecule), the term values of Li^*F and BeF still do not agree. The discrepancy is attributed to the very different spatial extension of the cores of Z^* and Z+1 in the case of the lightest atoms. This not only results in a considerably different equilibrium bond length of all analogous states but also in specific energy corrections to the valence states, which are difficult to predict without full ab initio calculations. It should be interesting to investigate the heavier alkali halide molecules, to which the Z+1 Analogy Model is predicted to apply.

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Table Captions

Table 1a	Position (in eV) of the maxima detected in the spectrum of molecular LiF
Table 1b	Position (in eV) of the maxima detected in the spectrum of molecular LiCl
Table 2	Vertical term values and orbital energies ε of BeF and Li^*F (in eV)
Table 3	Equilibrium bond lengths (in Å) and vibrational quanta (in eV) for BeF and Li^*F. $C = \sqrt{\mu_{BeF}/\mu_{LiF}}$, thus $C\omega_{BeF}$ is directly comparable to ω_{LiF}. The experimental data for BeF have been taken from reference 40.
Table 4	Vertical Li 1s ionization potentials (in eV) for the Li-halides.

Table 1a

peak	energy (eV)	peak	energy (eV)
a	56.86±0.04	j	62.30±0.05
b	57.00±0.04	k	62.43±0.05
c	57.07±0.04	l	62.63±0.05
d	59.22±0.06	m	62.82+0.05
e	59.36±0.04	n	63.35±0.05
f	59.52+0.03	o	63.53±0.05
g	59.68±0.03	p	63.72±0.05
h	60.56±0.04	q	63.88±0.05
i	61.63±0.05		

Table 1b

peak	energy (eV)	peak	energy (eV)
a	57.53±0.05	n	62.17±0.08
b	57.66±0.05	o	62.34±0.08
c	57.77±0.05	p	62.75±0.06
d	57.88±0.05	q	62.86±0.05
e	58.00±0.05	r	62.99±0.05
f	59.43±0.08	s	63.13±0.05
g	59.54+0.04	t	63.26±0.05
h	59.63±0.04	u	63.69±0.07
i	59.74±0.04	v	63.81±0.07
j	59.86±0.04	w	63.96±0.07
k	59.96±0.04	x	64.09±0.07
l	60.99±0.09	y	64.23±0.07
m	62.05±0.08	z	66.25±0.15

Table 2

optical orbital	BeF, R=1.36 Å exp.	theor.	R=1.56 Å BeF exp.	BeF$^+$ ε theor.	exchange corr. BeF exp.	BeF$^+$ ε theor.	Li*F theor.	exp.
column	1	2	3	4	5	6	7	8
$n=2\sigma^*$	9.1	9.27	9.4	9.40	8.5	8.53	7.77	8.6
$n=2\pi^*$	5.0	4.80	5.5	5.24	5.1	4.86	5.06	6.1
$\Delta(\sigma^*-\pi^*)$	4.1	4.47	3.9	4.16	3.4	3.67	2.71	2.5
3s	2.95		3.0	2.94	2.9	2.79		3.0
$3p_\sigma$	2.85		2.8	2.62	2.7	2.53		
$3p_\pi$				1.99		1.94		1.9

Table 3

unpaired valence electron	BeF exp. R_e (Å)	BeF exp. c·ω(eV)	Li*F theor. R_e (Å)	Li*F theor. ω(eV)	Li*F exp. ω(eV)	Li*Cl exp. ω(eV)
			1.56	0.14	0.113	0.082
$n=2^+$ (σ)	1.36	0.17	1.52	0.18	0.13	0.12
$n=2^+$ (π)	1.39	0.16	1.55	0.18	0.15	0.11
3s	1.33	0.18			0.18	0.13
3p	1.33	0.19			0.18	0.13
ion	(1.33)	(0.19)	1.49	0.18	(0.18)	(0.13)

Table 4

	LiF	Li_2F_2	LiCl	Li_2Cl_2
experimental	65.6±0.5		65.9±0.5	
theoretical	65.63±0.1	64.46±0.2	(65.9±0.1)	(65.4±0.2)

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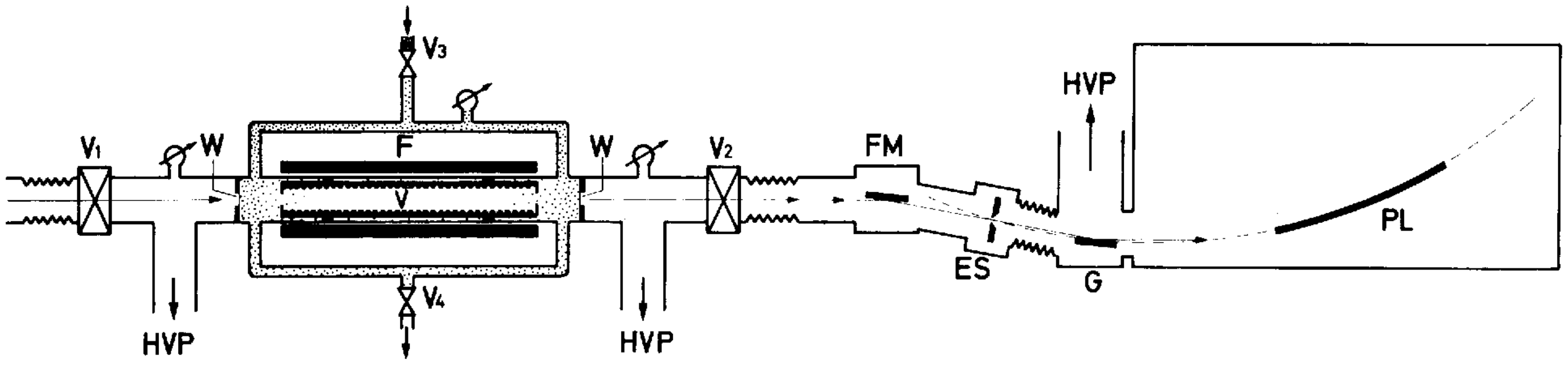
Figure Captions

Fig. 1 Outline of the experimental arrangement. V_1, V_2 valves; V_3 buffer gas inlet; V_4 buffer gas outlet; HVP to high vacuum pump; W thin film window, F furnace; V alkali-halide vapour column; FM focussing mirror; ES entrance slit; G grating; PL photographic plate.

Fig. 2a Li K-absorption of molecular and crystalline LiF.

Fig. 2b Li K-absorption of molecular and crystalline LiCl.

Fig. 3 Vertical orbital energy diagram of BeF^+ ($\sim$LiF), $BeCl^+$ ($\sim$LiCl), and $BeLiF_2^+$ ($\sim Li_2F_2$).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V₄
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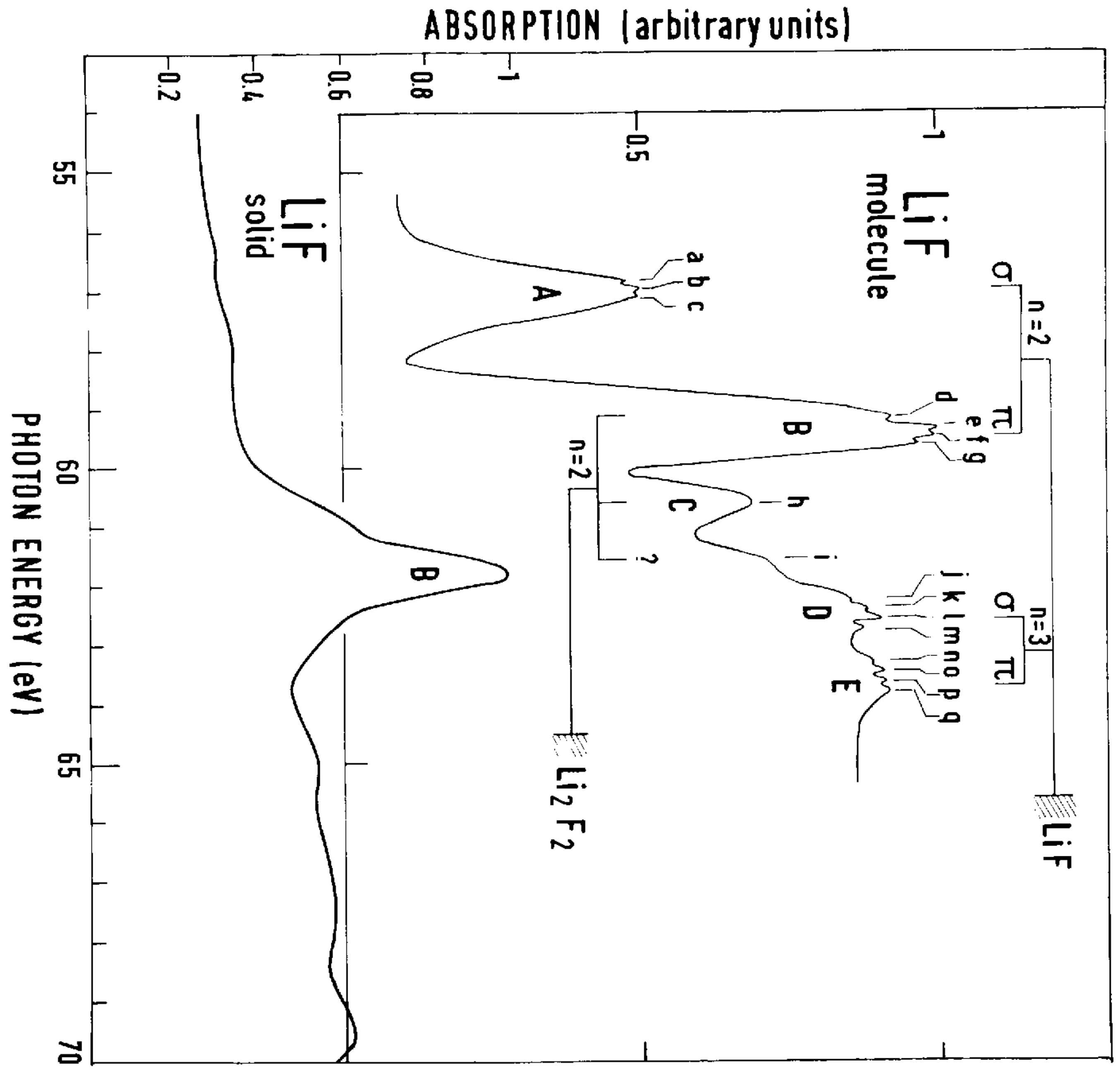
HVP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PHOTON ENERGY (eV)
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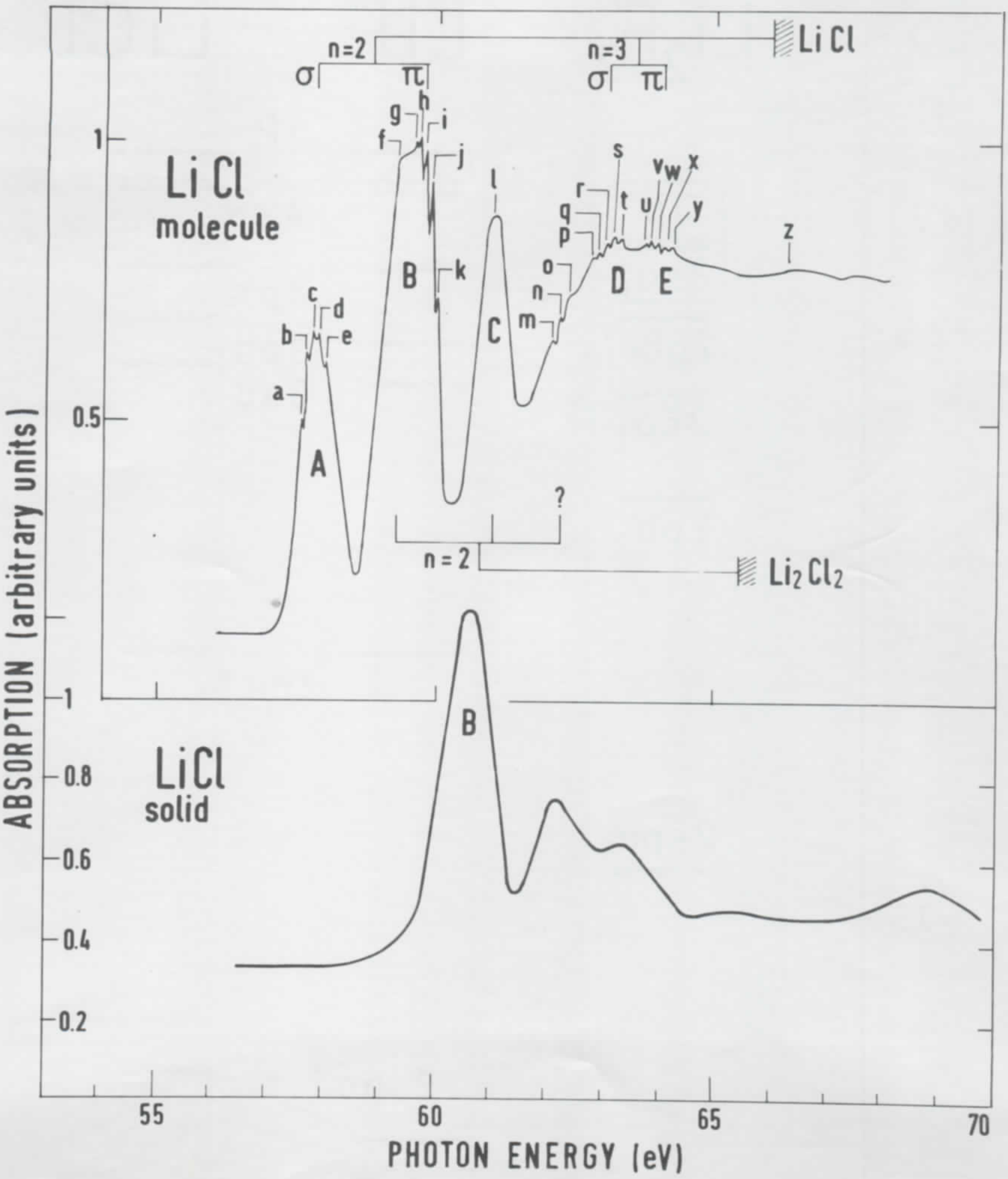
60
65
70
0.2
0.4
0.6
0.8
1
0.5
1
LiF molecule
LiF solid
A
B
C
D
E
B
a b c
d
e f g
h
i
j k l m n o p q
σ
π
n=2
n=3
σ
π
n=2
?
LiF
Li2 F2


n=2
σ
π
n=3
σ
π
Li Cl
1
Li Cl
molecule
g
h
f
i
j
l
s
r
t
u
v
w
x
y
q
p
z
o
B
k
n
D
E
c
d
b
e
m
C
a
0.5
A
?
n = 2
Li_2Cl_2
ABSORPTION (arbitrary units)
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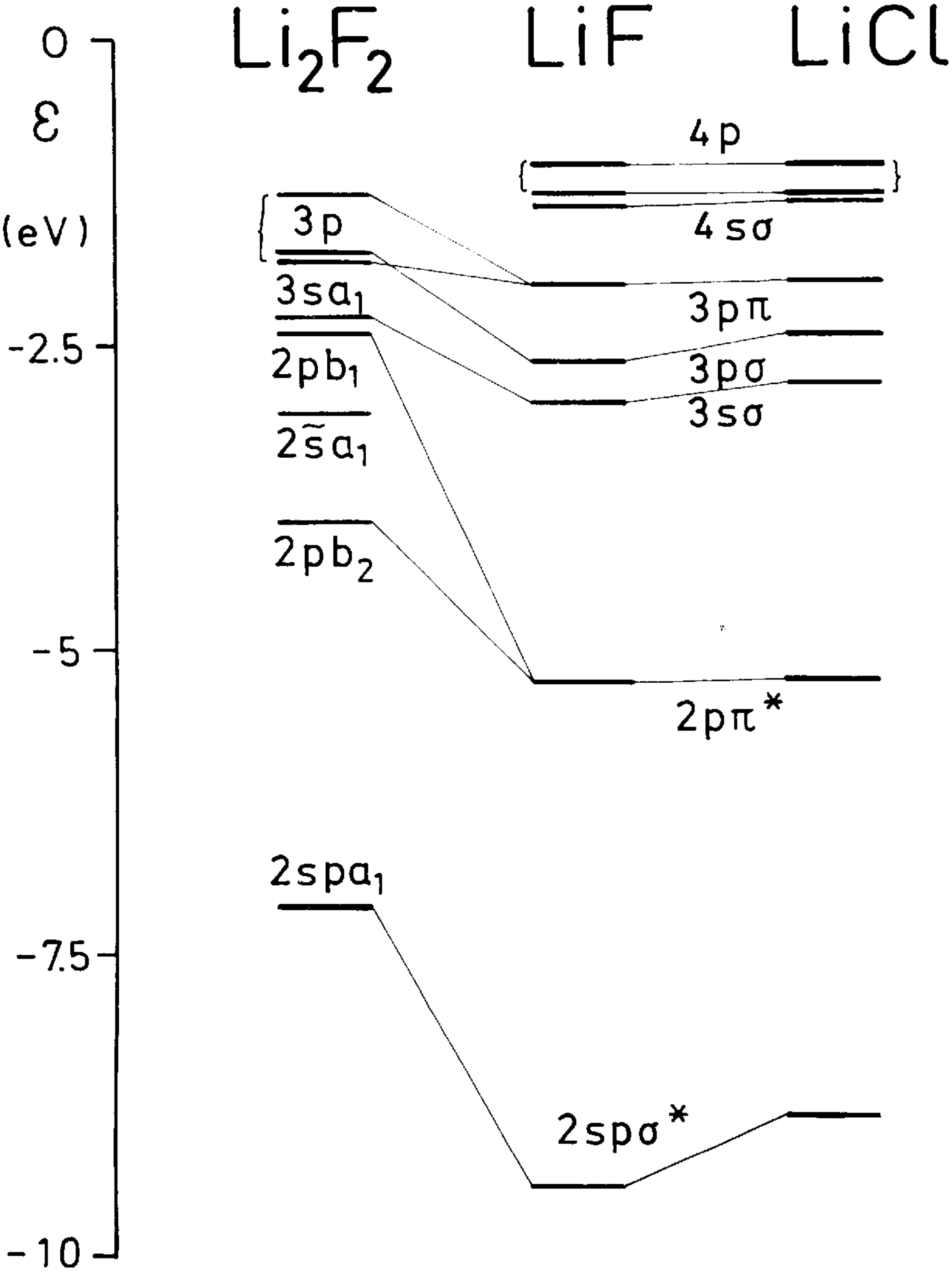
B
LiCl
solid
0.8
0.6
0.4
0.2
55
60
65
70
PHOTON ENERGY (eV)



Li$_2$F$_2$
LiF
LiCl
0
ε
(eV)
-2.5
-5
-7.5
-10
4p
4sσ
3p
3sa$_1$
2pb$_1$
2$\tilde{s}$a$_1$
2pb$_2$
3pπ
3pσ
3sσ
2pπ*
2spa$_1$
2spσ*