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The Electronic and Geometric Structure of the Free XeF_6 Molecule

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The absorption spectrum of gas phase XeF_6 *(from Ljubljana Fluor Chemistry Institute) was investigated in the region from 50 to 170 eV using the synchrotron radiation of DESY. We did not succeed in finding further evidence for the electronic isomeres hypothesis of Goodman. Our spectrum is fully explained if we assume that at room temperature* XeF_6 *consists of only one molecular species of slightly distorted* O_h*-geometry (Bartell and Gavin model). Nearly all other experimental results are consistent with this.*

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1. Introduction

Although XeF_6 has been known for more than ten years[1] and has in the meantime been intensively investigated, its geometric and electronic structure is still open to question.[2-4] This is not only a problem in itself but is of general theoretical interest too.

Xenon has 8 electrons in its closed valence shell (n=5), and each fluorine ligand contributes 1 active valence electron. From these 14 valence electrons 6 Xe-F bonding pairs may be formed, 1 lone pair remaining. According to the valence electron pairs repulsion model of Gillespie[5], this lone pair (which can approximately be described by a doubly occupied Xe 5sp hybrid orbital) will be located somewhere between the F-ligands and give rise to a strongly distorted octahedral symmetry, maybe of polar C_{3v} type.

The "theories of directed valence" of Kimball or Hansen[6], based on valence bond-models, are difficult to apply to this molecule, but also seem to predict a distorted geometry (of D_{3d} or lower symmetry).

Another model for predicting molecular geometries is the molecular orbital (MO)-model. Starting with the highest symmetry, i.e. O_h, the 14 valence electrons have to be filled into the following MO's, built up from Xe 5s, 5p and $F2p_\sigma$-AO's: bonding a_{1g} and t_{1u}, nonbonding e_g and antibonding a_{1g}, which is the highest occupied MO (HOMO). This results in a state of A_{1g} symmetry. There is no first order distortion and the expected geometry is O_h.

The same result is obtained by the ligand field theory. Here XeF_6 is described as $Xe^{6+}\ F_6^-$. The electronic ground state configuration of the central ion is $5s^2$, which cannot give rise to a first-order Jahn-Teller distortion of an octahedral ligand arrangement.

In the next section we refer to the experimental results on XeF_6 concerning its geometric and electronic structure. In section 3 we explain how XUV-absorption spectroscopy can be used to decide between the remaining possible alternatives of the structure. In section 4 we describe our experiment. In section 5 the experimental spectrum is interpreted and conclusions on the structure of XeF_6 are drawn. In section 6 a quantitative analysis of the spectrum at 66 eV is given.

2. Experimental Evidence

Several thorough and extensive investigations on the molecular structure of XeF_6 have been published.

1. Electron scattering by Bartell and Gavin[2]: The results are difficult to interpret. Under the explicit assumption that the gas is not a mixture of several geometric isomeres, the authors reached at the conclusion that the mean of the instantaneous molecular configurations is a slightly distorted O_h configuration in the broad vicinity of C_{3v}. The bending modes must be very anharmonic, soft and coupled to each other. It could not be decided whether O_h is a minimum or a saddle point of a strongly anharmonic potential surface.

2. Molecular beam experiments by Falconer, Klemperer et al.[7]: No electric or magnetic dipole moments were measurable. As a consequence no significant amount of XeF_6 can exist in a static deformed configuration with a non-zero moment. The rotation or inversion barrier between equivalent polar configurations should not exceed the order of $h\omega$. This result is strongly opposed to the Gillespie model.[5]

3. IR and Raman spectra by Claassen et al.[3]: Many more frequencies are reported than expected for an O_h-molecule vibrating harmonically. (This holds too if one does not extract as many different frequencies from the experimental

spectra as the authors do.) This may be explained by Bartell and Gavin's[2] model or by that of Goodman[3,4] which assumes that the XeF_6 vapor is a mixture of three non-polar geometric isomeres differing in electronic state and molecular geometry.

4. Visible and UV-absorption spectra by Claassen et al.[3]: The results are slightly temperature dependent. From this as well as from the marked temperature dependence of the Raman spectra[3], the authors concluded that the substance consisted of a mixture of different species in thermodynamic euqilibrium, the corresponding energy differences being about 500 cm^{-1}. This is what to be expected for Bartell and Gavin's model: the different species are vibrationally excited and should strongly differ in their Raman spectra because of the anharmonicity of the potential surface. But the experimental findings also seem not to be in conflict with Goodman's hypothesis, although the differences in the electronic excitation spectra of the different species are smaller than one would expect for different electronic species. However, that the changes of the spectra were lagging in time by several minutes behind the changes in temperature seems especially to support the molecular isomeres hypothesis, although these temperature effects as well as those in the matrix spectra[3] are difficult to interpret convincingly in any case. Especially, it is difficult to understand, why no time lags where detectable in the IR measurements[3].

For both models of the structure of XeF_6 one can give theoretical arguments[2,3].

1. If the molecule becomes distorted the occupied orbitals are allowed to mix with virtual orbitals, which were of different species in O_h. This mixing will be strongly symmetry dependent. These second order corrections give a potential surface which may be of the shape required by the Bartell model. Semiempirical calculations seem to support this view (e.g. Ref. 2 and references given therein).

2. On the other hand, the first excited electronic state of the molecule, described as "5s5p" ^3P in the ligand field model, is expected to have a rather low energy. As the "5p" orbital is degenerate and strongly antibonding, the triplet state will be subject to a strong linear Jahn-Teller distortion. It might therefore be possible that the "$5s^2$" ^1S ground state with O_h geometry and the Jahn-Teller stabilized component of the first excited triplet with strongly distorted geometry are very near in energy and both thermally populated, as postulated by Goodman[3,4].

There are, however, two difficulties with this alternative.

1. Basch et al.[8] have calculated the first vertical singlet-triplet a_{1g} - "5p" excitation energies of XeF_2, XeF_4 and XeF_6 to be 4.2, 4.0 and 2.0 eV. The real values will be larger because of the correlation error in the ground state and the error in the calculated HOMO energies. The first absorption bands found experimentally are broad and weak with maxima near 5.4, 4.8/5.4 and 3.7 eV, respectevily.[3]

   It seems reasonable therefore to assign these bands to the above mentioned singlet-triplet excitations. From the XUV-spectra of XeF_2 and XeF_4[9] we know that the 5p orbital may undergo a Jahn-Teller stabilization of approximately 1 - 2 eV. Thus one expects an energy of about 2 eV for the lowest triplet of XeF_6, but not an energy near 0.1 eV as presumed by Goodman.[4]

2. There are two Jahn-Teller-active vibrational modes: The e_g and the t_{2g} vibration stabilizing the D_{4h} and D_{3d} symmetries. In Fig. 1 we show a correlation diagram for the states arising from ^3P under the action of an octahedral ligand field (V_{O_h}), a perturbation of D_{3d} symmetry ($V_{D_{3d}}$) and spin-orbit coupling (λ). A distortion to D_{4h} symmetry will lead to nearly the same diagram, with "oblate" and "prolate" interchanged. In any case the lowest state is A_{1u}, which has zero magnetic moment, in accordance with the

experiment of Code et al.[7]. However, the Jahn-Teller stabilization energy is certainly larger than the spin-orbit splitting constant (our estimate is $\lambda \gtrsim 0.9$ eV). As a result, the $A_{1u} - E_u$ energy difference will be small, not larger than kT, i.e. the strong Jahn-Teller effect - which is the necessary assumption for the electronic isomeres model - quenches the spin-orbit splitting, so that there should occur a spin magnetism one order of magnitude larger than the sensibility of the apparatus of Code et al.

Obviously, both arguments are not firm enough as to disprove Goodman's hypothesis. Therefore a decisive experiment to answer the question, whether there is a significant amount of XeF_6 electronically excited at room temperature, is still necessary.

3. XUV Spectroscopy on XeF_6

Such an experiment would measure the XUV absorption in the 140 eV region ($\lambda \sim 90$ Å).

The "$5s^2$" $^1A_{1g}$ ground state of XeF_6 will show no light absorption due to the excitation of a Xe 4p core electron. The only empty orbital in the valence shell is the Xe "5p" orbital, but 4p → 5p is Laporte-forbidden. From XeF_2 and XeF_4 we know that vibronic interaction is not strong enough to make this transition detectable. Excitations into higher Rydberg orbitals will also not occur, as (according to the pseudopotential model of Nefedow and Dehmer[11]) the potential barrier produced by the fluorine atoms prevent any overlap between the inner and the Rydberg orbitals. The same conclusion is obtained from analogy with SF_6[8] or by experimental extrapolation: in Xe and XeF_2 there are only weak 4p → 6s transitions, which are hardly detected in XeF_4[6].

The situation is quite different, if there is some amount of "5s5p" ^3P states in the XeF_6 gas (according to Goodman[4] over 50 % at room temperature). Then 4p → "5s" transitions are possible which should be much more intense than the 4p → 6s transitions in Xe or XeF_2. According to the measured chemical shifts of the xenon core orbital energies in Xe, XeF_2, XeF_4, XeF_6[9,12], we expect the Xe 4p ionization potential in XeF_6 to be 153.5 eV. The 4p → "5s" transitions should lie 10 - 15 eV lower in energy, i.e. near 140 eV.

4. Experimental Details

The substance was obtained from the Fluorine Chemistry Laboratory of Institute Jozef Stefan, Ljubljana, and was IR-spectroscopically pure. The general experimental setup was analogous to our XeF_2 and XeF_4 investigation[9]. The inner surface of the apparatus has been passivated by treatment with ClF_3. The substance was contained in a stainless steel vessel, from which the vapor was pumped so slowly through the absorption cell, that a possible thermal equilibrium between electronic isomeres could be reached if the relaxation time would be smaller than 10 minutes. No absorption lines which might be due to Xe, XeF_2, XeF_4 or other impurities were recorded; this we take as evidence for the purity of the substance in the absorption cell.

5. The Experimental Result

Figure 2 shows the XeF_6 absorption coefficient in arbitrary units from 50 to 170 eV. The structured band between 62 and 72 eV is given on a larger scale in Fig. 3.

In the region about 140 eV we failed to detect any structure. This result is strongly contrary to the electronic isomeres model.

As expected we did not measure any 4p → Rydberg type absorption bands at or above 150 eV, nor 4d → Rydberg bands between 72 and 75 eV. Between these two regions there is a broad hump with maximum near 100 eV, caused by the 4d → εf ionization, with very similar shape to the Xe, XeF_2 and XeF_4 absorption in this energy range.[12] The structured band at 67 eV will be analysed in more detail in section 6. Here we only state the result: The band can fully be explained if it is assigned to the "$4d^{10}5s^2 \rightarrow 4d^9 5s^2 5p$" transitions. No additional structure could be found in this energy region as predicted, if one applies the electronic isomeres hypothesis. In this context we mention that neither Brundle et al.[13] nor Berkowitz et al.[14] found corresponding additional structure in their photoelectron and photoionization mass spectra of XeF_6.

The whole 4d-excitation spectrum is superimposed on a continuum which rises strongly at lower energies. This underlying spectrum is steadly increasing from Xe (where it is nearly zero) through XeF_2 and XeF_4[6] to XeF_6 and is attributed to the ionization of valence electrons, mainly the fluorine 2p ones.

6. Xe 4d → "5p" transitions

In this section we will give a quantitative analysis of the absorption near 66 eV (Fig. 3), which we describe as Xe 4d → "5p" transitions.

1. Siegbahn[12] has measured the Xe 4d ionization potential of XeF_6 and obtained 75.4 eV and 77.4 eV for the 5/2 and 3/2 spin-orbit components. The accuracy of these values is 0.2 eV, which is less than the difference between Siegbahns values for XeF_2 and XeF_4 and those obtained by extrapolation of the corresponding XUV-Rydberg spectra[9]. The spin-orbit splitting in the free xenon atom is 1.97 eV and is only very slightly reduced in XeF_2 and XeF_4[9]. Thus we assume 1.9 eV for XeF_6. From the chemical shift Siegbahn deduces an effective

charge of 1/3 on each fluorine ligand. With this value it is possible to reproduce the 4d ligand field splittings in XeF_2 and XeF_4 by the point charge model; for XeF_6 one obtains a value of 0.06 eV. The ab initio SCF value is $\Delta = 0.15$ eV, however in XeF_2 and XeF_4 the ab initio values were too large by a factor of nearly 2. Therefore the 4d ligand field splitting parameter is assumed to be smaller than 0.1 eV. Only the $d_{5/2}$ level is split (into u'_g and e''_g), with a splitting of less than 0.06 eV which may be neglected.

2. The vertical one electron energy of the Xe 5p type empty orbital may be extrapolated from the XUV-spectrum of XeF_2 and XeF_4 as near 9.9 eV for XeF_6. There is no direct ligand field splitting at this level. The 5p spin-orbit splitting of Xe^+ is 1.31 eV. According to the population analysis of Basch[8], we expect only a value of 2/3 of this for the molecule, i.e. 0.9 eV.

3. With these assumptions concerning the initial and final MO's and within the one-electron model we expect three absorption lines as sketched in Fig. 4. The relative intensities are given in parenthesis. Whereas the energies roughly agree with the measured values of Fig. 3, there are large discrepancies in the intensities. According to the degeneracies of the $d_{5/2}$ and $d_{3/2}$ levels one at first expects an intensity ratio for the $d_{5/2}$ to $d_{3/2}$ excitations of 1.5 , which indeed is meaured in the 4d → Rydberg spectra of Xe, XeF_2, XeF_4. However, for the 4d → 5p transitions one measures an intensity ratio of 1.2 for XeF_2, 1.0 for XeF_4 and 0.5 for XeF_6. This steady change can be explained if we take the electronic interaction into account. In Fig. 5 we present an intermediate coupling diagram for XeF_2. The intensity ratio of the lower to higher energy line groups is 3 : 2 = 1.5 for zero electronic interaction, but

2 : 3 = 0.67 for zero spin-orbit interaction. Taking both interactions as well as the ligand field effect (V_{lig}) of the fluorine atoms into account, we calculate an intensity ratio of 1.3 (measured 1.2).

In the XeF_4 the situation is very similar: The fluorine ligand field reduces the $4d_{5/2}$ to $4d_{3/2}$ excitation intensity ratio from 1.5 to 1.4. Inclusion of electronic interaction lowers it down to 1.0, which is just the measured value. (Vibronic coupling only affects the line shape of the two bands but not their intensity ratio[16].)

Figure 6 shows the intermediate coupling diagram for XeF_6: the intensity ratio becomes zero in the case of zero spin-orbit interaction (left side), so that we do not worry about the low calculated (0.65) and measured (0.5) intensity ratio for XeF_6. Furthermore, the transition energies are shifted. The new values compare better with the measured values of Fig. 2, being too large by only 0.2 eV. This means that one should use 10.1 eV for the vertical "5p" orbital energy instead of the extrapolated value of 9.9 eV. Finally we remark that it is not necessary to take into account specific energy shifts or intensity changes caused by Jahn-Teller effect as in the case of XeF_4[15], since the Jahn-Teller active orbital in XeF_6 is not of e but of t type.

In this context it is interesting to discuss the analogous problem of the inverted $S2p_{3/2} \rightarrow$ "3s" to $2p_{1/2} \rightarrow$ "3s" intensity ratio in SF_6[15] (measured 0.8 instead of 2.0). This is rather simple as there are only two allowed transitions. In Fig. 7 we have plotted the energy difference as well as the intensity ratio versus K/λ (K = singlet-triplet splitting, λ = spin-orbit splitting). Contrary to the level splitting the intensity ratio is strongly dependent on the exchange interaction and again goes down to zero for large K (or small λ) because of the singlet-triplet selection rule.

Finally we would like to give a comment on the line widths of the three bands in Fig. 3. The measured values are 0.9 ± 0.1 eV, this is nearly the same as in XeF_2 and XeF_4, where it was possible to explain it semiquantitatively by vibronic broadening. If the effect is mainly caused by a_{1g} and e_g vibrational modes, the value of the Jahn-Teller stabilization should not strongly exceed 1 eV, which we assume as typical for XeF_2 and XeF_4. If, however, the line-width is mainly caused by the very weak and anharmonic t_{2g} vibration, the Jahn-Teller stabilization had to be much larger and might be of the order necessary for the electronic isomeres hypothesis. But then the absorption peaks should show a triplet structure with pronounced right and left side shoulders[16], which were not detected (see Fig. 3).

Summarizing, the absorption bands in Fig. 3 behave exactly as expected for a $4d^{10}5s^2 \rightarrow 4d^9 5s^2 5p$ excitation under O_h or nearly O_h symmetry.

7. Conclusion

In our experiment we could find no evidence that the XeF_6 vapor in our absorption cell should contain considerably more than one per cent of electronically excited species with strongly distorted geometry: we did not find any $4p \rightarrow 5s$ absorption bands as predicted for distorted XeF_6 and the absorption bands at 66 eV can be explained as an excitation in a molecule with O_h-symmetry.

If nevertheless the electronic isomeres hypothesis should be the correct one, we must conclude that

1. the molecules evaporating from solid XeF_6 at room temperature are all of the $5s^2\ {}^1A_{1g}$ species with O_h geometry and
2. the rate constant of rearrangement into 5s5p with a distorted geometry

must be smaller than 0.001/sec. From this follows an activation energy of at least 2/3 eV, which seems not to be unreasonable in the case of a Jahn-Teller stabilization of about 3 eV. However, these values seem very large. GCF calculations for checking this are in progress.

Concluding there exist several difficulties with the electronic isomeres hypothesis. The only indication for it which is not interpretable within the model of Bartell and Gavin, are the time lags often seen by Claassen et al.[3], but not in all of their experiments.

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Figure Captions

Fig. 1 Schematic energy level diagram of a sp ^3P term under the action of an octahedral field (V_{O_h}), a perturbation of D_{3d} symmetry ($V_{D_{3d}}$) and spin-orbit coupling (λ).

Fig. 2 Absorption cross section of gaseous XeF_6 in arbitrary units at room temperature vs photon energy in the range 50 to 170 eV.

Fig. 3 Absorption cross section of XeF_6 in the energy range from 62 to 72 eV.

Fig. 4 Xe 4d → 5p excitation of XeF_6 in the one-electron scheme. Energy values in eV, relative intensities in paranthesis.

Fig. 5 The 4d → "5p" excited configuration of XeF_2 in intermediate coupling. Left side without spin-orbit coupling (ΛS-coupling), right side without electronic exchange interaction ($\Omega\omega$-coupling). The thickness of the connecting lines indicate the relative transition intensities, numbers being given for the limiting cases only.

Fig. 6 The 4d → "5p" excited configuration of XeF_6 in intermediate coupling. Left side without spin-orbit coupling (LS-coupling), right side without interelectronic interaction (jj-coupling). Only the $j = 1$ (T_{1u}) states can be reached from the $j = 0$ (A_{1g}) ground state and are shown in the figure. The numbers give the relative transition intensities for the limiting cases and for XeF_6. The corresponding transition energies are given in parenthesis.

Fig. 7 Line-splitting $\Delta E/\lambda$ and intensity ratio I_2/I_1 for $p^6 - p^5s$ excitation vs K/λ (K = singlet-triplet splitting, λ = spin-orbit splitting). The mark on the abscissa corresponds to the estimated K/λ value of SF_6.

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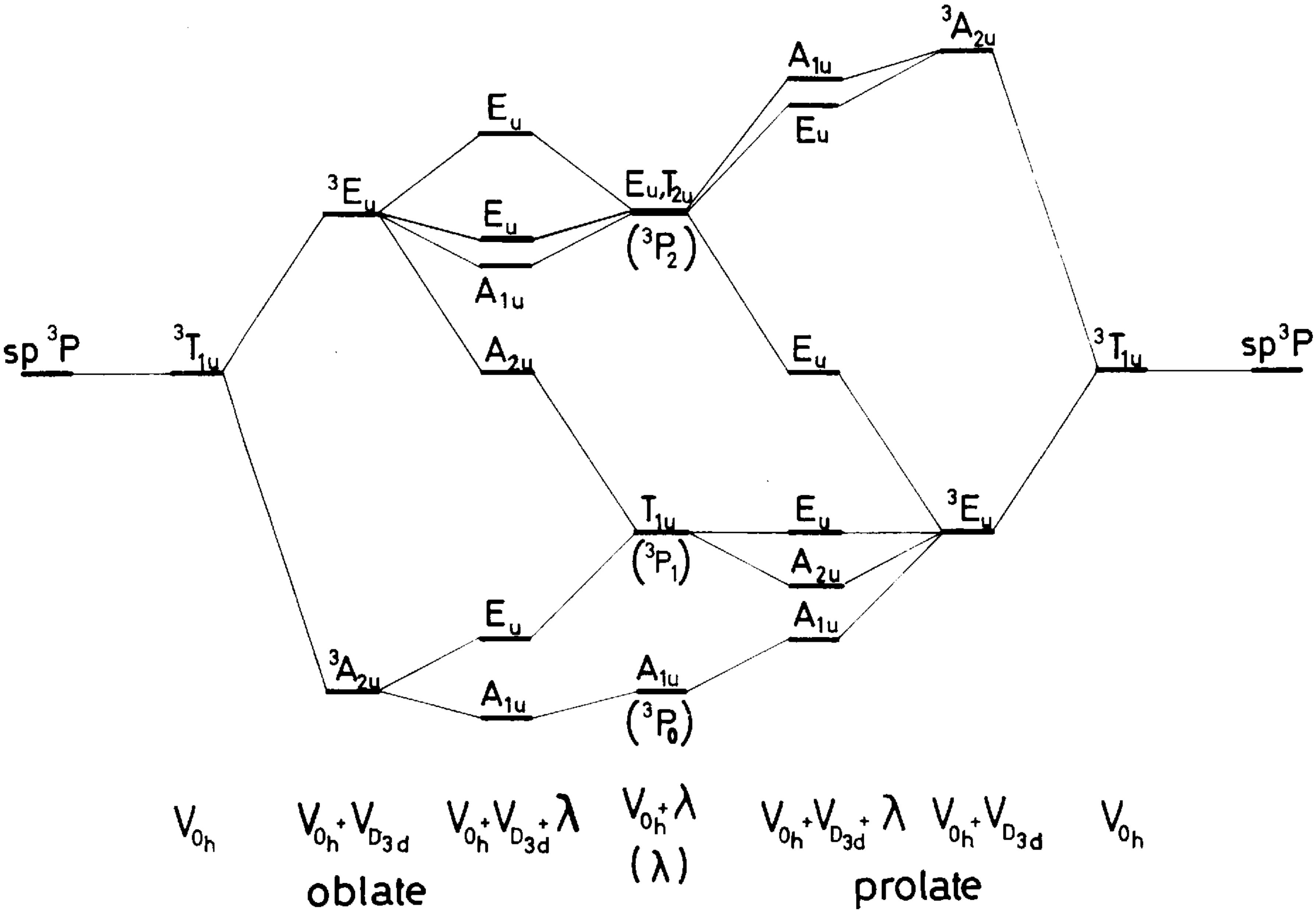
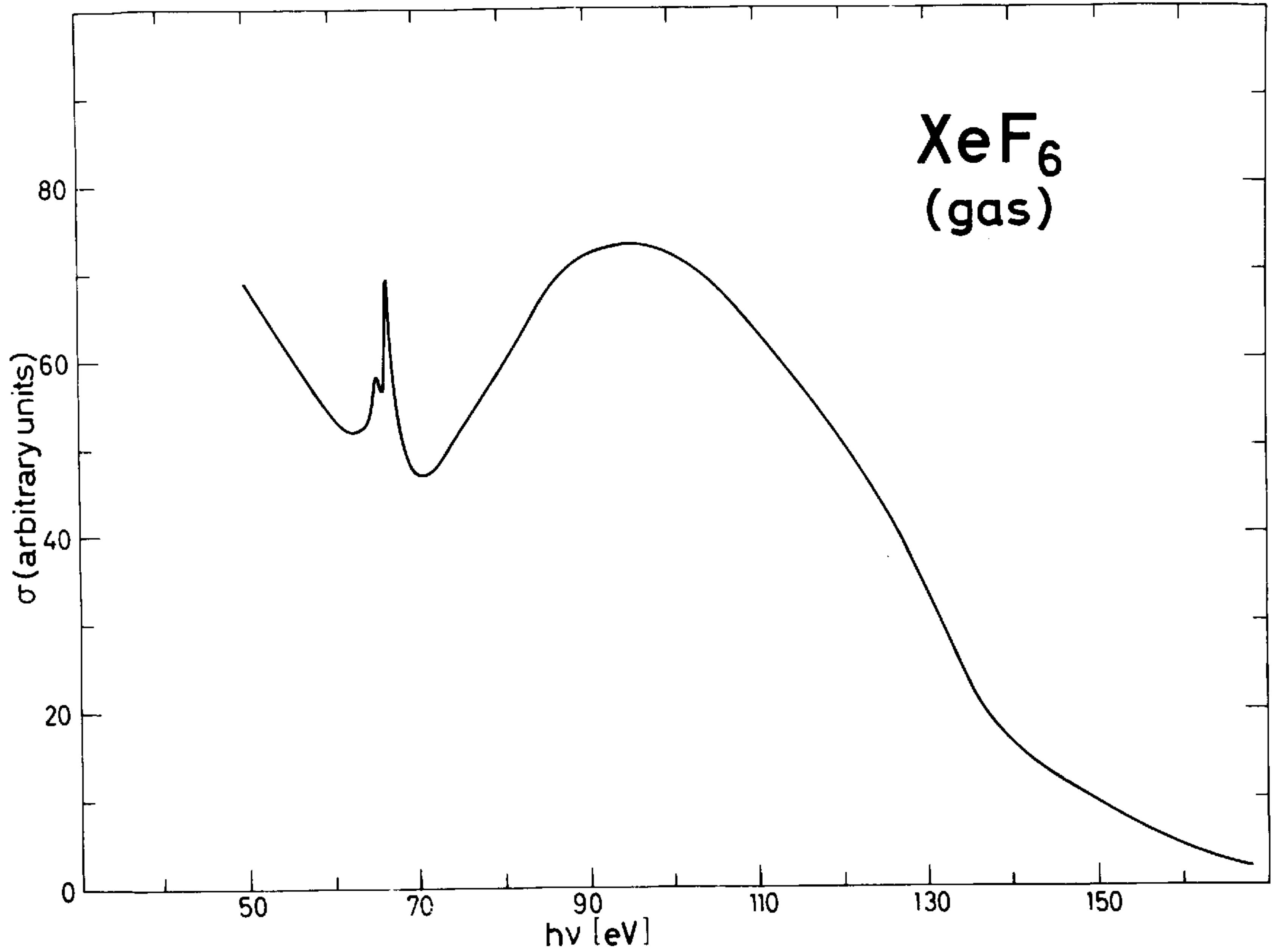


sp ^{3}P
^{3}T$_{1u}$
^{3}E$_u$
^{3}A$_{2u}$
E$_u$
E$_u$
A$_{1u}$
A$_{2u}$
E$_u$
A$_{1u}$
E$_u$,T$_{2u}$
(^{3}P$_2$)
T$_{1u}$
(^{3}P$_1$)
A$_{1u}$
(^{3}P$_0$)
A$_{1u}$
E$_u$
E$_u$
E$_u$
A$_{2u}$
A$_{1u}$
^{3}A$_{2u}$
^{3}E$_u$
^{3}T$_{1u}$
sp^{3}P
V$_{0_h}$
V$_{0_h}$+V$_{D_{3d}}$
V$_{0_h}$+V$_{D_{3d}}$+λ
V$_{0_h}$+λ
(λ)
V$_{0_h}$+V$_{D_{3d}}$+λ
V$_{0_h}$+V$_{D_{3d}}$
V$_{0_h}$
oblate
prolate

Fig. 1



XeF_6
(gas)
σ (arbitrary units)
0
20
40
60
80
50
70
90
110
130
150
hν [eV]

Fig. 2

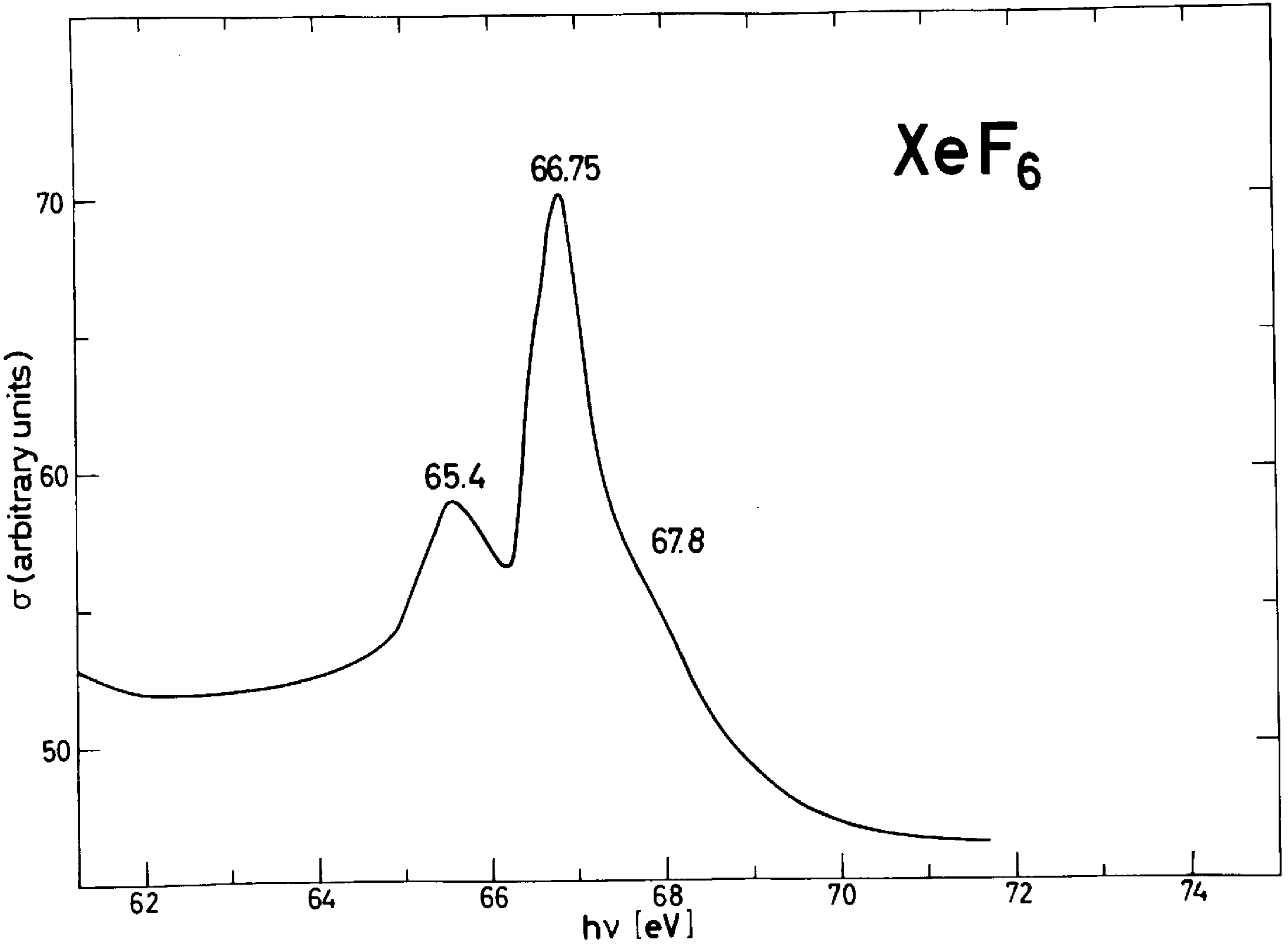

XeF$_6$
66.75
65.4
67.8
σ (arbitrary units)
70
60
50
62
64
66
68
70
72
74
hν [eV]

Fig. 3

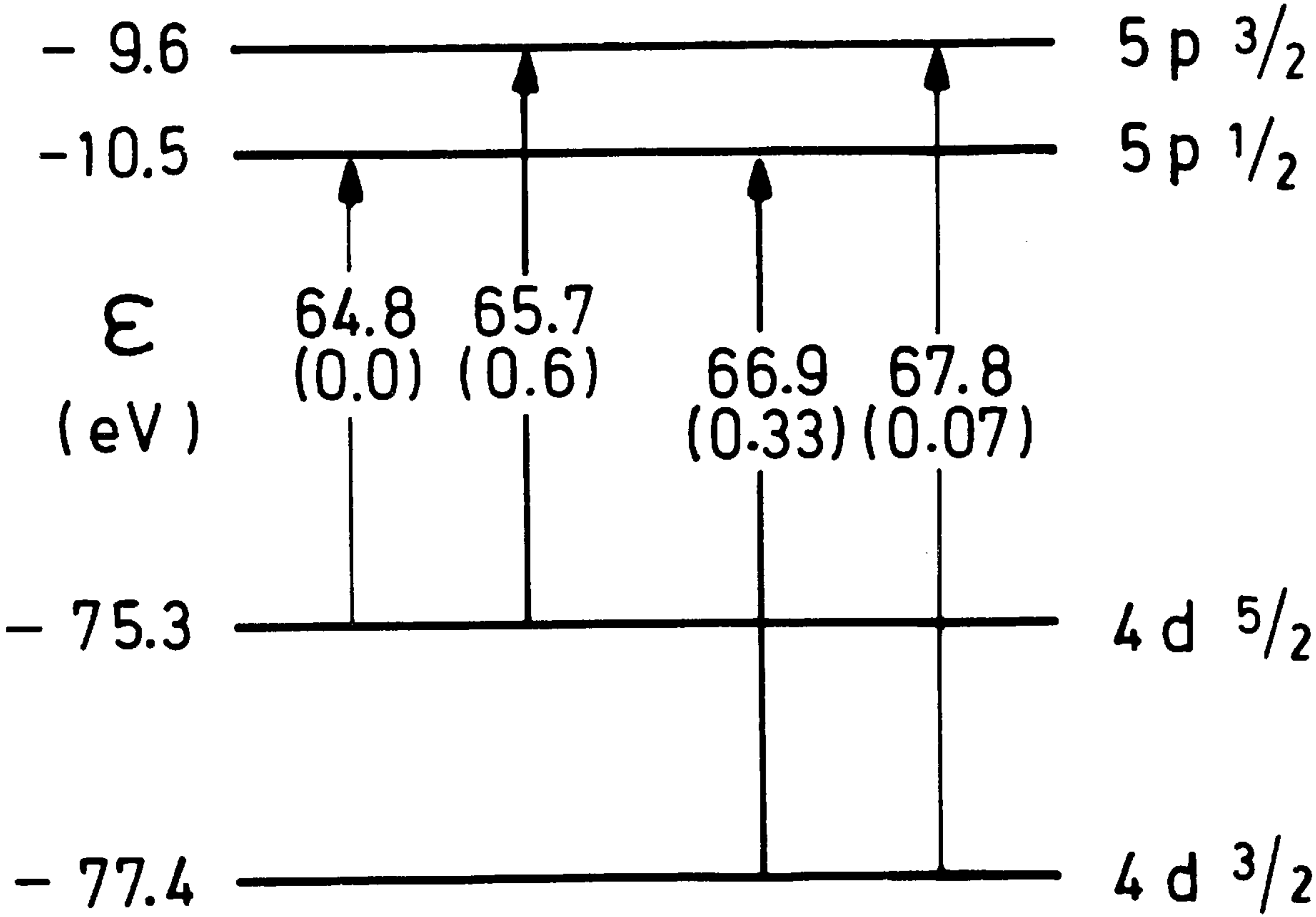
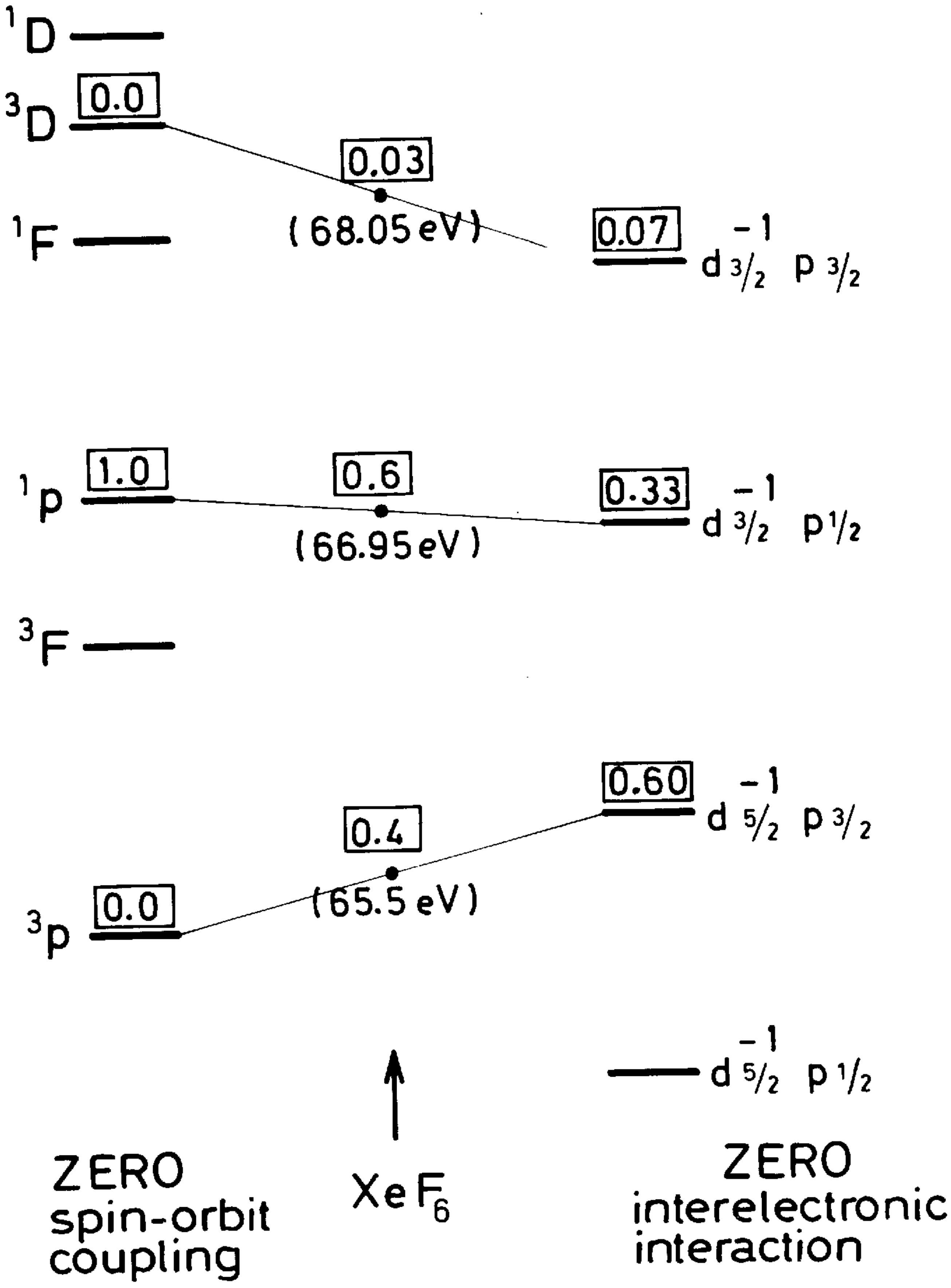

- 9.6
-10.5
- 75.3
- 77.4
5 p $^3/_2$
5 p $^1/_2$
4 d $^5/_2$
4 d $^3/_2$
ε
(eV)
64.8
(0.0)
65.7
(0.6)
66.9
(0.33)
67.8
(0.07)

Fig. 4



¹D
³D
0.0
0.03
(68.05 eV)
¹F
0.07
d 3/2 -1 p 3/2
¹p
1.0
0.6
(66.95 eV)
0.33
d 3/2 -1 p 1/2
³F
0.60
d 5/2 -1 p 3/2
0.4
(65.5 eV)
³p
0.0
d 5/2 -1 p 1/2
ZERO spin-orbit coupling
XeF6
ZERO interelectronic interaction

Fig. 5

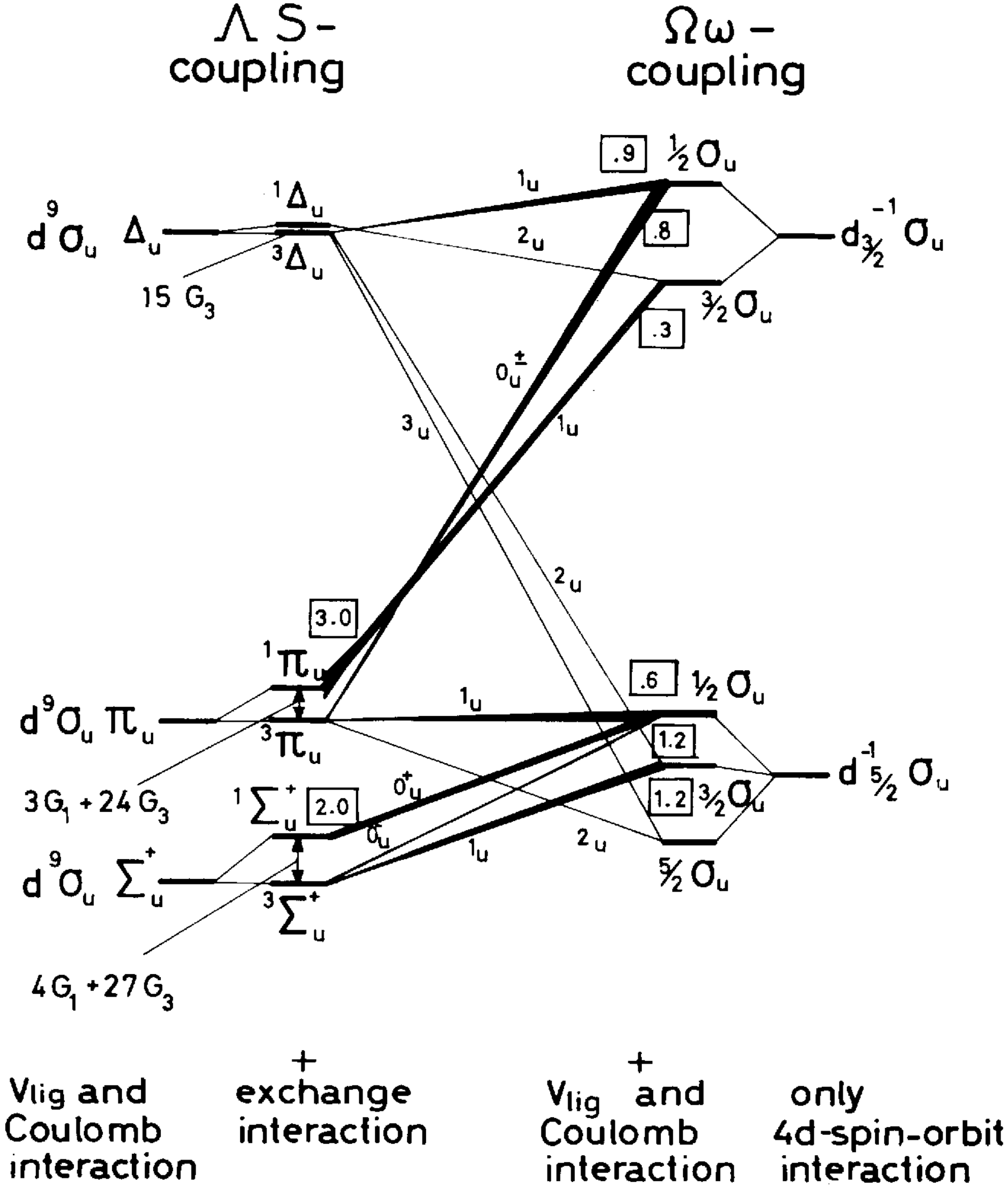

ΛS-coupling
Ωω-coupling
$d^9\sigma_u\ \Delta_u$
$^1\Delta_u$
$^3\Delta_u$
$15\,G_3$
1_u
2_u
3_u
$0_u^\pm$
.9
$\frac{1}{2}\sigma_u$
.8
.3
$\frac{3}{2}\sigma_u$
$d^{-1}_{3/2}\,\sigma_u$
1_u
2_u
3.0
$^1\pi_u$
$d^9\sigma_u\,\pi_u$
$^3\pi_u$
$3G_1+24G_3$
1_u
.6
$\frac{1}{2}\sigma_u$
1.2
1.2
$\frac{3}{2}\sigma_u$
$d^{-1}_{5/2}\,\sigma_u$
$^1\Sigma_u^+$
2.0
0_u^+
0_u^-
1_u
2_u
$\frac{5}{2}\sigma_u$
$d^9\sigma_u\ \Sigma_u^+$
$^3\Sigma_u^+$
$4G_1+27G_3$
Vlig and Coulomb interaction
+ exchange interaction
+ Vlig and Coulomb interaction
only 4d-spin-orbit interaction

Fig. 6

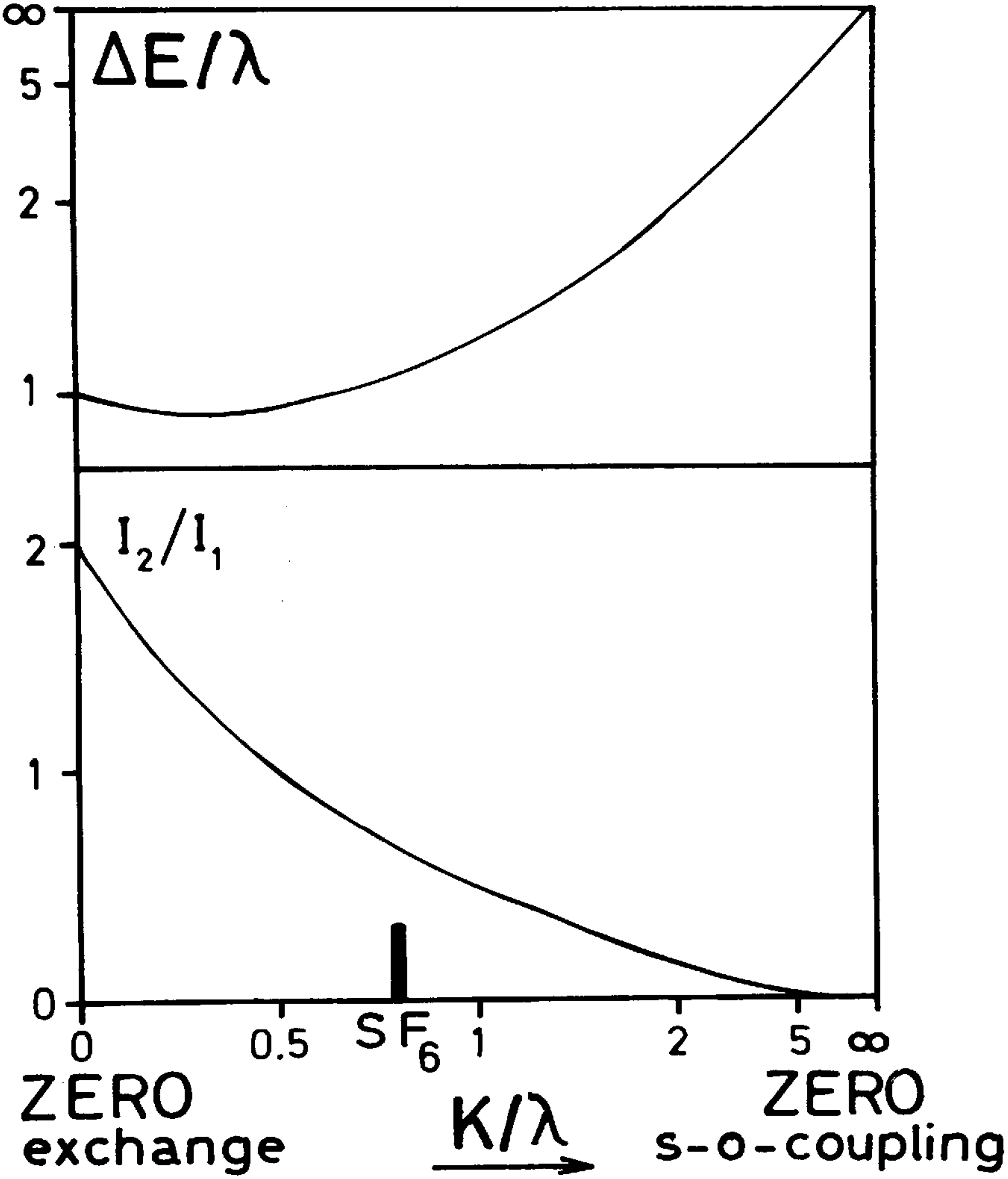

ΔE/λ
∞
5
2
1
I₂/I₁
2
1
0
0
0.5
SF₆
1
2
5
∞
ZERO
exchange
K/λ
ZERO
s-o-coupling

Fig. 7