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Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada, N6A 5B7, and Institute of Physics, Uppsala University, S-751 21 Uppsala 1, Sweden

Gas-Phase ESCA Studies of Valence and Core Levels in XeF$_2$ and XeF$_4$

G. M. BANCROFT,*[1a] P.-Å. MALMQUIST,[1b] S. SVENSSON,[1b] E. BASILIER,[1b] U. GELIUS,[1b] and K. SIEGBAHN[1b]

Using monochromatized Al Kα radiation, we have made a detailed gas-phase ESCA study of the valence levels and Xe 3d and 4d core levels in XeF$_2$ and XeF$_4$. The valence band peaks have been assigned to the molecular orbitals previously calculated. Several previous experimental and theoretical assignments are shown to be incorrect. Agreement is generally good between our observed positions and intensities and the calculated values. The observed broadening of the compound Xe 3d and 4d peaks (relative to the corresponding Xe gas peaks) is shown to be due to the C_2^0 asymmetry term in the ligand field expansion. The broadening of the 4d levels of 0.12 ± 0.02 eV (XeF$_2$) and 0.19 ± 0.02 eV (XeF$_4$) leads to a 4d$_{3/2}$ splitting of 0.33 ± 0.04 eV (XeF$_2$) and 0.40 ± 0.04 eV (XeF$_4$). These values are in excellent agreement with the d$_{3/2}$ splittings derived in previous absorption studies. The derived C_2^0 terms [+0.041 ± 0.004 eV (XeF$_2$) and −0.045 ± 0.004 eV (XeF$_4$)] are also in excellent agreement with those previously determined. The average 3d broadening of 0.06 ± 0.02 eV for the two compounds leads to a 3d$_{3/2}$ splitting of 0.18 ± 0.06 eV and a $|C_2^0|$ value of 0.021 ± 0.006 eV. These are in good agreement with the normalized theoretical values. The anomalous electron spectrum in the 4s-4p range was found to change upon fluoridization. Similar effects are seen when the nuclear charge is changed and can be qualitatively explained in terms of the energy difference between doubly ionized states and the unperturbed 4p hole state.

Introduction

Several recent papers have reported gas-phase ESCA[2] and UV (He I and He II) photoelectron[3,4] spectra of the xenon fluorides. In addition, there has been considerable interest in the absorption spectra of these compounds.[5,6] An ab initio SCF MO calculation[7] has been useful for assigning parts of the valence band spectra[3,4] and for calculating the observed[5] ligand field splitting of the Xe 4d levels in XeF$_2$ and XeF$_4$.

However, a number of ambiguities still exist in the valence band assignments, and the valence levels above 18 eV binding energy have not been observed and/or unambiguously assigned. There is also confusion about the role of ligand field splitting on core levels in these and other spectra. Ligand field broadening and splitting,[8] due to the asymmetry crystal field term C_2^0, has been observed recently in the photoelectron spectra of Sn and Cd 4d levels.[9] A similar Xe 4d splitting was also reported in the absorption studies of XeF$_2$ and XeF$_4$.[5] However, Carroll et al.[2b] ruled out ligand field splitting of the Xe 3d lines as being unimportant in 3d line broadening. In contrast, Basch's calculations,[7] Gupta and Sen's calculations,[8] and previous experimental results on Sn compounds[10] indicated that the 3d ligand field splitting should approach half of the 4d ligand field splitting.

In addition to the above xenon fluoride results, there have been recent ESCA studies of the interesting 4p region of the xenon gas spectrum.[11,12] The apparent absence of the 4p$_{1/2}$ peak is due to configuration interaction of 4d^{8}5s^{2}5p^{6}nl states with the 4p single hole state. The nature of this 4p spectrum should change appreciably with the number of F ligands.

We have undertaken a high-resolution ESCA study of the 3d, 4d, and valence band levels of XeF$_2$ and XeF$_4$ with three objectives: to clear up the ambiguities in the assignment of the valence levels, to measure accurately the ligand field

broadening of both the 3d and 4d Xe core levels, and to examine changes in the 4p structure. We also derive cross section ratios which are compared with current theoretical values and comment on differences in chemical shifts for the 3d and 4d orbitals.

Experimental Section

The gas-phase spectra of XeF$_2$ and XeF$_4$ were recorded using the electrostatic ESCA instrument,[13] which incorporates a fine-focusing monochromatized Al Kα x-ray source and multidetection system. The compounds were purchased from L'Air Liquid in France, and high-purity Xe gas was used as reference. To prevent extensive decomposition of the fluorides, all handling of the compounds was done in an Ar-filled drybag, and all inlet parts of the spectrometer were coated with Teflon spray. In this way, we were able to obtain spectra of the fluorides free of the decomposition products in a relatively short time. The intense 3d core levels were often monitored during the accumulation of the valence band spectra to ensure that no decomposition to Xe gas was occurring. For the Xe 3d and 4d line width studies, we ran spectra of xenon gas and the compound simultaneously. A number of high-quality spectra were accumulated for these core levels to provide good statistical data.

The spectra were computer fitted using standard iterative methods to Gaussian and/or Gauss–Lorentz combination functions. When Gauss–Lorentz functions were used for the core levels, statistically acceptable χ^2 values (the sum of the squares of the deviations from the best fit divided by the variances) were obtained. For example, for the XeF$_2$ (and Xe) 4d spectra, χ^2 values of ~150 (~130 degrees of freedom) were obtained.

Results and Discussion

Valence Band Spectra. The valence band region of the XeF$_2$ and XeF$_4$ electron spectra is illustrated in Figure 1. Assignments, binding energies, and intensity data are given in Table I. The theoretical binding enegies in Table I are 0.92 times the calculated orbital energies, a figure found
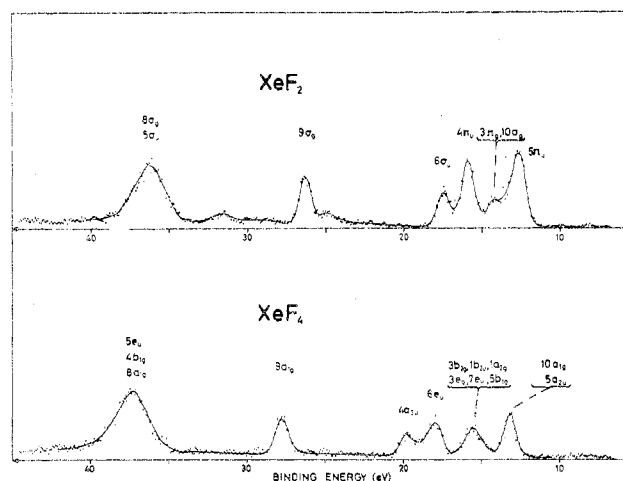
Figure 1. Valence electron spectrum of XeF_2 and XeF_4.

previously[3,4] to be a suitable correction to the Koopmans theorem approximation to electron binding energies. The theoretical intensities have been calculated using the intensity model.[11] In this model, the intensity of the jth molecular orbital I_j^{MO} is proportional to

$$I_j^{MO} \propto \sum_{A, \lambda} (2 + \beta_{A\lambda}^{AO}/2)(P_{A\lambda})_j \sigma_{A\lambda}^{AO} \tag{1}$$

assuming an angle of $\pi/2$ between the nonpolarized x-ray beam and the emitted photoelectron. $\sigma_{A\lambda}^{AO}$ is the total photoionization cross section of an atomic $A\lambda$ orbital, $\beta_{A\lambda}^{AO}$ is the corresponding atomic asymmetry parameter, and $(P_{A\lambda}^{AO})_j$ is the "probability" of finding in the jth molecular orbital an electron belonging to the atomic $A\lambda$ orbital. We have calculated the relative I_j^{MO} values using the Mulliken population analysis given by Basch[7] as approximate $P_{A\lambda}$ values and the $\sigma_{A\lambda}^{AO}$ and $\beta_{A\lambda}^{AO}$ values given recently by Scofield,[14] Nefedov et al.,[11c] and Kennedy and Manson.[15]

In fitting the XeF_2 spectrum, we were able to obtain a good fit by constraining the intensity ratios of the first five peaks to their theoretical values and the widths to be equal. The five positions obtained from this fit (Table I) are in excellent agreement with those derived earlier.[3] For XeF_4, the intensities and positions were not fixed, and yet our positions relative to the positions (or centroid of positions) obtained earlier[4] are again in excellent agreement up to 17.5 eV binding energies. The above agreement in both positions and intensities strongly suggests that the previous assignments[4] up to 17.5 eV are correct. In particular, the intensity information for XeF_2 indicates that the $5\pi_u$ band is at lower binding energy than the $10\sigma_g$ band, in contrast to the theoretical assignment.[7] It should be realized for both XeF_2 and XeF_4 (next paragraph) that the MO calculations were performed on the ground states and not on any ion states. Differential relaxation effects could well lead to such different orderings between theory and experiment.

Above 17.5 eV binding energies, we are able to clarify previous discrepancies and complete the valence band assignments. In XeF_2, the $9\sigma_g$ peak is at 26.28 eV, and it is apparent that the previous tentative assignment of the $9\sigma_g$ peak at $\approx$22.5 eV is incorrect. Similarly, the previous tentative assignments of the $9a_{1g}$ and $4a_{2u}$ peaks in XeF_4 are incorrect. Moreover, our intensity data suggest that the $6e_u$ and $4a_{2u}$ orbitals have an ionization ordering different from the ground-state ordering or that these orbitals are inverted in the ground-state theoretical calculation. Thus, our assignment in Table I of $6e_u < 4a_{2u}$ gives good agreement between observed and predicted intensities. It should also be noted that except for the $6e_u$ peak, there is reasonable agreement between
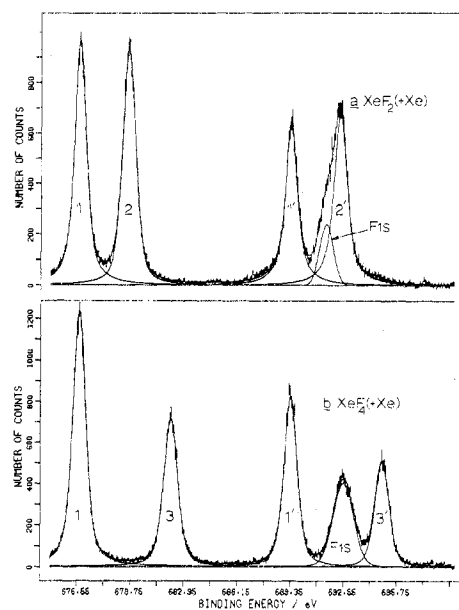

Figure 2. The 3d core electron spectrum of Xe (peaks 1 and 1′), XeF_2 (peaks 2 and 2′), and XeF_4 (peaks 3 and 3′). Observe that the binding energy increases from the left.
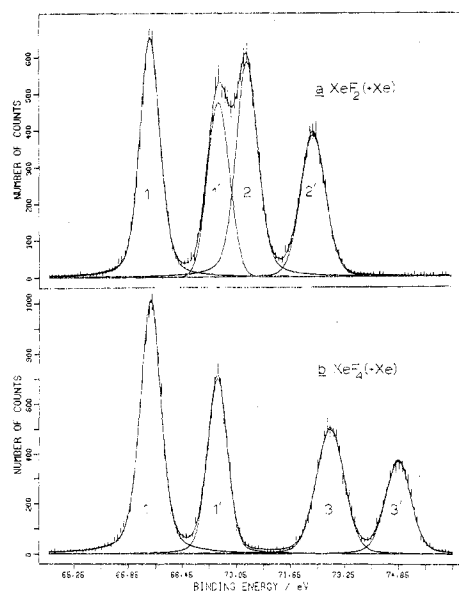

Figure 3. The 4d core electron spectrum of Xe (peaks 1 and 1′), XeF_2 (peaks 2 and 2′), and XeF_4 (peaks 3 and 3′). Note that the binding energy increases from the left.

theoretical and observed positions. Although the observed intensities agree very well with the theoretical up to 20 eV binding energies, the observed intensities are considerably smaller than the theoretical for the high binding energy peaks. For the F 2s peaks at least, the high theoretical values are at least partly due to the 100% F 2s character assumed for these peaks. The F 2s character will be substantially less than this, leading to smaller theoretical intensities.

The 3d and 4d Core Level Spectra. The Xe 3d and 4d spectra of the compounds (along with Xe gas) are shown in Figures 2 and 3, and the computed parameters are given in Table II. The excellent reproducibility of the relative positions and widths resulted in the very small *external* standard deviations. For these spectra, the *internal* standard deviations (obtained from the least-squares fitting procedure) for a *single* position or width was never larger than 0.04 eV, except when the peaks strongly overlapped. The similarity of the averaged internal and external deviations[16] is a strong indication that

Table I. Valence Electron Spectral Parameters (eV) for XeF_2 and XeF_4

	XeF₂						XeF₄				
	Binding energies			Intensities			Binding energies			Intensities	
	Exptl		Theor[a]				Exptl		Theor[a]		
Orbital	This work	Ref 3	Ref 7	Exptl[b]	Theor	Orbital	This work	Ref 4	Ref 7	Exptl	Theor
$5\pi_u$	12.65	12.42	12.51		1	$10a_{1g}$	⎱13.22	13.1	11.7	⎱1	⎱1
		12.89				$5a_{2u}$	⎰	13.4	13.9	⎰	⎰
$10\sigma_g$	13.62	13.65	11.79		0.17	$5b_{1g}$		14.5	15.2		
$3\pi_g$	14.33	14.35	14.71		0.20	$1a_{2g}$		15.1	15.8		
$4\pi_u$	15.87	15.60	15.92		0.74	$7e_u$	⎰15.55	(15.4)	16.2	0.97	0.98
		16.00				$1b_{2u}$		15.8	16.5		
$6\sigma_u$	17.39	17.35	16.93		0.34	$3e_g$		(16.0)	16.6		
$9\sigma_g$	26.28	≈22.5[c]	25.24	0.46	1.0	$3b_{2g}$		16.3	16.8		
$5\sigma_u$	⎱36.23	Not obsd	37.10	⎱1.49	⎱2.7	$6e_u$	18.08	17.9	19.6[c]	1.04	1.2
$8\sigma_g$	⎰		37.20	⎰	⎰	$4a_{2u}$	19.74	18.4?[c]	19.0[c]	0.67	0.70
						$9a_{1g}$	27.79	19.8[c]	27.4	0.82	1.5
						$5e_u$	⎱		39.2	⎱	⎱
						$4b_{1g}$	⎰37.40	Not obsd	38.6	⎰3.64	⎰8.4
						$8a_{1g}$	⎰		40.0	⎰	⎰

[a] 0.92 times the theoretical values[7] as given by Brundle.[3,4] [b] The intensities of the first five peaks were constrained to covary at their theoretical ratios. [c] Previous assignment incorrect—see text.

Table II. Core Level ESCA Parameters (in eV) for XeF_2 and XeF_4

			Xe parameters						F 1s parameters	
Compd	Level	No. of spectra	Binding energy[a]	Chem shift[a]	Spin–orbit splitting	Width	Difference in width	Area ratio	Binding energy	Width
XeF₂	4d	4	70.34 (2)	2.84 (1)	1.98 (2)	0.76 (2)	0.12 (2)	1.42 (2)		
			72.32 (1)							
	3d	3	679.63 (1)	2.93 (1)	12.68[c]	0.92 (1)	0.05 (2)	1.41 (1)	691.4 (2)	1.04 (4)
			692.31 (1)	2.96						
	4p	1	148.54 (5)	3.03 (5)		1.16				
	4s	1	216.04 (10)	2.72 (10)		2.4				
XeF₄	4d	3	72.80 (1)	5.30 (1)	2.00 (1)	0.88 (2)	0.19 (2)	1.43 (1)		
			74.80 (1)	5.32 (1)						
	3d	4	682.20 (1)	5.50 (1)	12.68 (1)	1.02 (1)	0.06 (1)	1.43 (1)	692.52 (3)	1.39 (4)
			694.88 (1)	5.53						
	4p	1	151.27 (5)	5.76 (5)		1.17				
	4s	1	218.66 (10)	5.34 (10)		2.7				

[a] Binding energies were calibrated using Xe gas and the Xe binding energies given in ref 12. For the 3d peaks of Xe gas the spin–orbit splitting determined is 12.68 ± 0.01 eV, in good agreement with 12.65 ± 0.08 eV determined by Gelius.[11] [b] The difference in width between the compound line widths and Xe gas line widths. [c] Constrained at this value.

our standard deviations are meaningful.

The Gauss fractions[16] for the Xe 4d lines (0.85 for XeF₂ and XeF₄ and 0.70 for Xe) were substantially larger than those for the 3d levels (0.45 for XeF₂ and XeF₄ and 0.30 for Xe). The large Gauss fractions are expected for the very narrow (~0.1 eV)[12] 4d levels, and the lower Gauss fraction for the 3d levels is consistent with the very much larger inherent line width (~0.5 eV).

The binding energies and spin–orbit splittings are in agreement, within the errors, with those given previously[11] but are usually not in so good agreement (relative to the quoted errors) with the 3d parameters given by Carroll et al.[2b] For example, the 3d shifts are 0.1 eV larger than those given by Carroll, and the spin–orbit splittings are ~0.1 eV smaller. In addition, the 3d spin–orbit splitting for XeF₄ is not smaller then the Xe value as reported by Carroll.[2b]

There is, however, a suggestion that the 4d spin–orbit splitting in XeF₄ is slightly larger than that in Xe gas, and this will be rationalized shortly. It is also apparent that the chemical shifts for the 4d levels are smaller than those for the 3d levels. This is expected from a ground-state SCF calculation for Xe, which results in the k value of 14.4 eV for the 3d level, substantially larger than the corresponding value of 13.4 eV for the 4d level. Similar "second-order" chemical shifts have been observed recently.[17,18,19]

Cross section ratios derived from our data are in good agreement with ratios calculated from Scofield's cross sections.[14] Thus, the observed $\sigma_{3d_{3/2}}$:$4\sigma_{F1s}$ ratio, derived from the

XeF₄ spectrum, is 0.89 compared with the theoretical value of 0.85.[14] Similarly, the $d_{5/2}$:$d_{3/2}$ ratios given in Table II for both the 4d and 3d electrons are in good agreement with the theoretical values of 1.437 and 1.443, respectively.

The line widths are of particular interest. The Xe 4d lines in the fluorides broaden significantly (>0.1 eV) compared to the Xe gas lines, while the 3d lines broaden only a small (but significant) amount. Combined with the theoretical calculations[7] and the previously observed 4d ligand field splitting in these compounds,[5] our results are conclusive evidence that the great majority of *both* the 4d and 3d line broadening is due to ligand field splitting from the C_2^0 asymmetry term in the crystal field expansion.

XeF₂ and XeF₄ are known to be linear and planar molecules, respectively, in both the solid and gas phase (see references in ref 5). For XeF₂ ($D_{\infty h}$ symmetry) the ligand field potential includes C_2^0 and C_4^0 terms; while for XeF₄ (D_{4h} symmetry), the ligand field potential includes C_2^0, C_4^0, and C_4^4 terms. Basch's calculation,[7] and experimental evidence,[5,9] suggests that the C_4 terms are negligibly small. The Hamiltonian for the description of the $4d^9$ (or $3d^9$) state for both molecules becomes

$$\mathcal{H} = 3C_2^0(L_z^2 - 2) + \lambda[{}^1/_2(L_+S_- + L_-S_+) + L_zS_z] \qquad (2)$$

The spin–orbit $d_{3/2}$ and $d_{5/2}$ levels are split into two and three, respectively, by the ligand field term.[9,10]

Because we have a precise knowledge of the Xe gas and compound 4d line widths, we can obtain a quite accurate

estimate of $d_{3/2}$ splittings by fitting the $d_{3/2}$ envelopes with two peaks of equal area with the Xe gas line width and shape. Such fits give a $d_{3/2}$ splitting of 0.33 ± 0.04 eV for XeF_2 and 0.40 ± 0.04 eV for XeF_4. These values are in remarkably good agreement with the $d_{3/2}$ splittings given by Comes et al.[5] of 0.35 and 0.37 eV, respectively.[5,20] As for the chemical shifts, these observed splittings are about 65% of the theoretical values.[7]

From the above splittings, and the known[21] positive (XeF_2) and negative (XeF_4) nuclear electric field gradients (proportional to C_2^0),[8-10] we derive C_2^0 values of +0.041 ± 0.004 eV for XeF_2 and −0.045 ± 0.004 eV for XeF_4. These similar $|C_2^0|$ values are expected from the similar nuclear electric field gradients.[21,22]

The above excellent agreement between the normalized theoretical,[7] absorption,[5] and our ESCA ligand field splitting values strongly indicates that the great majority of the broadening is due to ligand field splitting. Broadening from vibrational effects[23] in these heavy molecules does not appear to be significant. This is not unexpected for three reasons: the vibrational energies[24,25] in these molecules are very small (≤ 0.07 eV), very narrow lines (~ 0.2 eV) were obtained in the 4d–6p absorption spectra of these compounds,[5] and very narrow core d lines (<0.1 eV) were observed for Zn[26] and Cd[9] compounds with similar vibrational energies.

As noted above, the 4d spin–orbit splitting, 2.00 eV in XeF_4, appears to increase from the Xe gas value of 1.98 eV. Using our C_2^0 values for XeF_2 and XeF_4 and calculating the spin–orbit splittings from the centroid of the $d_{3/2}$ and $d_{5/2}$ levels, we estimate that the *apparent* spin–orbit splittings for XeF_2 and XeF_4 should increase by about 0.01 eV from the atomic Xe value. These small increases are a further indication that even very large ligand fields will only slightly increase the apparent spin–orbit splitting.[9,27]

The 3d line broadenings are also consistent with those estimated from the C_2^0 ligand field splittings given by Basch.[7] The average broadening of the 3d levels in XeF_2 and XeF_4 leads to an average $3d_{3/2}$ splitting of 0.18 eV. At such small splittings, the line width is very insensitive to quite substantial changes in the splitting (ref 1, appendix D), and a rather large error of 0.06 eV results. The $|C_2^0|$ value calculated from this splitting is 0.021 ± 0.006 eV. The C_2^0 values calculated from Basch's results are +0.026 and −0.028 eV for XeF_2 and XeF_4, respectively. Taking 65% of these values yields C_2^0 values of +0.017 and −0.018 eV, respectively. These values are again in good agreement with those observed. Once again, the major cause of the 3d broadening[10] must arise from the ligand field splitting. The theoretical and our experimental results contrast with those given by Carroll et al.[2b] who estimated that the 3d splittings in XeF_2 and XeF_4 would be smaller than the 4d splittings by at least an order of magnitude.

The 4p Spectrum. The anomaly of the 4p ionization in atomic Xe has recently been discussed.[11,12,28,29] In the Xe gas-phase ESCA spectrum, the $4p_{1/2}$ line is completely smeared out, and what appears in low resolution as the $4p_{3/2}$ "line" consists of at least three components which are discernible at high resolution. The mechanism behind this anomaly is understood as an energy matching of the 4p single vacancy with discrete or continuous states containing a $4d^2$ double vacancy and an excited nl^* orbital. Disregarding second-order effects, the chemical shift of a $4d^2$ double vacancy should be approximately twice as large as that of a single 4p vacancy. Therefore, we may expect that the energy matching will be affected by adding fluorine ligands to the central Xe atom. Figure 4 shows the 4s–4p spectra of Xe, XeF_2, and XeF_4. A comparison with the 3d and 4d spectra shows that the "normal" shake-up contribution can be neglected. The differences in the Xe 4p spectra seems to be almost entirely
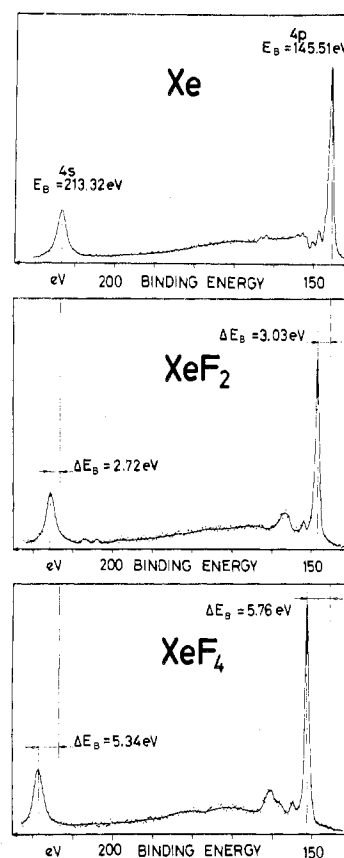

Figure 4. The 4s–4p core electron spectra of Xe, XeF_2, and XeF_4.

due to changes in the CI resonance structure. The relative energies of states containing a 4p vacancy and of states containing a $4d^2$ vacancy will be changed in the same direction by adding fluorine ligands to the central atom as by increasing the nuclear charge Z. If nl^* excited orbitals are little influenced by the ligand atoms, the XeF_2 and XeF_4 4p spectra should become increasingly similar to the atomic Cs or Ba 4p spectra. This also seems to be the case when Figure 4 is compared to Figure 5, which has been extracted from Figure 5 of ref 12.

From the chemical shifts of the main structures we may also draw some conclusions. Neglecting relativistic effects, etc., we have

$$E_B{}^{\text{exptl}} = E_B{}^{\Delta\text{SCF}} + \Delta E^c \tag{3}$$

where $E_B{}^{\text{exptl}}$ is the experimental binding energy of the line, $E_B{}^{\Delta\text{SCF}}$ is the unperturbed ΔSCF binding energy (which includes relaxation), and ΔE^c is the difference in correlation energy between the ion and the neutral system. Note that this energy is *negative* in the case of, e.g., the 4s line in Xe. For the chemical shifts we then get

$$\Delta E_B{}^{\text{exptl}} = \Delta E_B{}^{\Delta\text{SCF}} + \Delta\Delta E^c \tag{4}$$

In eq 4 $\Delta E_B{}^{\Delta\text{SCF}}$ is not known from calculations with sufficient accuracy. For the 3d and 4d levels of atomic Xe ΔE^c is known to be in the order of an electron volt.[12] $\Delta\Delta E^c$ should then be at least an order of magnitude smaller and is generally neglected. We may therefore put $\Delta E_B{}^{\Delta\text{SCF}} = \Delta E_B{}^{\text{exptl}}$ for the 3d and 4d levels. It should be noted that these shifts would be equal if no second-order effects were present.

To estimate $\Delta E_B{}^{\Delta\text{SCF}}$ for the 4s and 4p lines we note that the second-order chemical shift effect is, to a first approximation, a linear function of the binding energy in the energy range of the 3d–4d levels. This can be seen from atomic
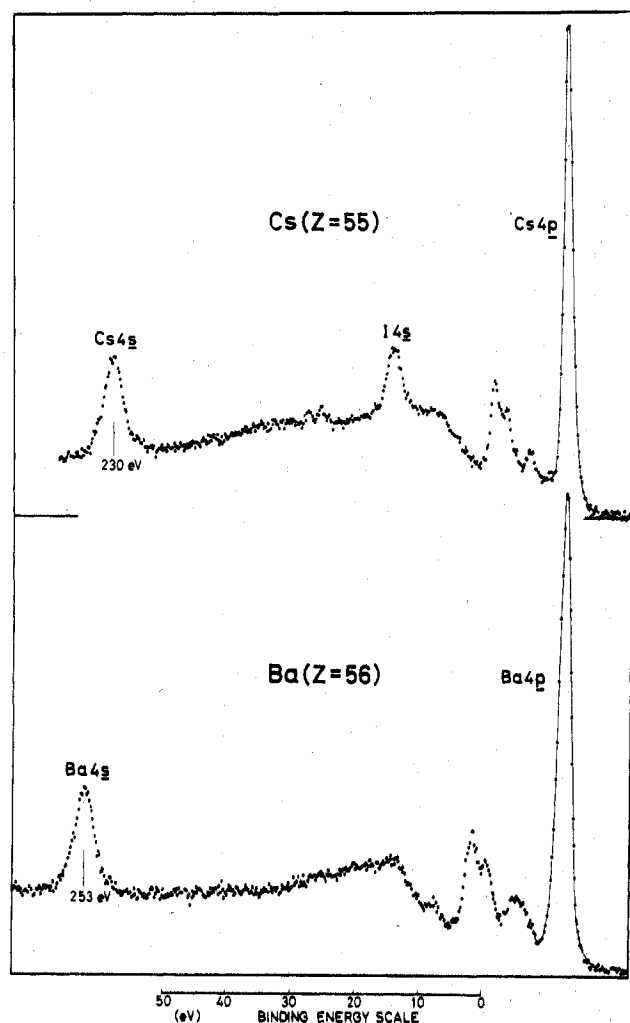
Figure 5. The 4s–4p core electron spectra of Cs and Ba. These elements correspond to an increase of the nuclear change of 1 and 2, respectively, compared to Xe.

calculations[30] and is also seen from the calculations by Basch et al.[7] From the values in Table II we consequently arrive at the estimated ΔSCF chemical shifts: $\Delta E_B^{\Delta SCF}(\text{XeF}_2, 4p) = 2.85$ eV, $\Delta E_B^{\Delta SCF}(\text{XeF}_2, 4s) = 2.86$ eV, $\Delta E_B^{\Delta SCF}(\text{XeF}_4, 4p) = 5.33$ eV, $\Delta E_B^{\Delta SCF}(\text{XeF}_4, 4s) = 5.35$ eV. After insertion of these values into eq 4 together with ΔE_B^{exptl} values from Table II we obtain the estimates for the changes in ΔE^c: $\Delta\Delta E^c(\text{XeF}_2, 4p) = 0.18 \pm 0.05$ eV, $\Delta\Delta E^c(\text{XeF}_2, 4s) = -0.14 \pm 0.1$ eV, $\Delta\Delta E_c(\text{XeF}_4, 4p) = 0.43 \pm 0.05$ eV, $\Delta\Delta E^c(\text{XeF}_4, 4s) = -0.01 \pm 0.1$ eV. Since ΔE^c is *negative* for the Xe 4s and Xe 4p levels, a positive $\Delta\Delta E^c$ corresponds to a decreased absolute value of

ΔE^c. The estimates above therefore indicate that the "4p line" in XeF₄ is less configuration mixed than in atomic Xe, whereas for the 4s line, ΔE^c is constant within error limits, indicating a constant configuration mixing.

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