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Theoretical and Experimental Shake-up Studies on the Xe Core Level ESCA of XeF_2

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By obtaining the ESCA of XeF_2 to high statistics, we have observed a number of satellites on the low-kinetic-energy side of the Xe 3d and 4d primary photolines. These satellites are attributed to shake-up. Using ground-state MO's for Xe and XeF_2, Rydberg levels for Xe and XeF_2 from the UV spectra, and the Xe gas shake-up spectrum, we have constructed a Xe 3d hole state MO diagram for XeF_2. The shake-up peaks have been assigned by using this MO diagram, and the calculated shake-up energies are generally in very good agreement with experiment. An SCF–Xα–SW calculation on the 3d hole state of XeF_2 provides further confirmation of our shake-up assignment. An SCF–Xα–SW calculation on the XeF_2 ground state gives good agreement with the experimental valence-band energies and intensities.

Introduction

Since the original preparation of a compound of xenon and fluorine in early 1962, there has been considerable interest in theoretical and spectroscopic studies of the xenon fluorides.[2] Detailed vacuum ultraviolet results on XeF_2, XeF_4, and XeF_6[3] have been obtained by Schwarz with synchrotron radiation. Recent gas-phase ESCA studies of the valence levels of XeF_2 and XeF_4[4] have clarified previous experimental and theoretical discrepancies and completed the valence-band assignments.[5] Theoretical calculations with the ab initio self-consistent-field molecular-orbital (MO) method[5b] and relativistic DV–Xα (discrete variational)[6] method have been reported recently.

As a continuation of our current core-level shake-up studies on the ESCA of inorganic and organometallic molecules,[7] we report in this paper the Xe 3d and 4d shake-up spectra of gaseous XeF_2. This molecule was chosen for a number of reasons. First, the UV spectra of both Xe and XeF_2 are well documented.[2,3] Second, the electron shake-up–shake-off spectrum of the Xe gas 3d levels has been reported[8] and is very useful in interpreting the more complicated XeF_2 shake-up spectra. Third, the molecular orbital scheme is relatively simple and well characterized.[4-6]

By use of theoretical SCF–Xα–SW calculations and an empirical atomic model, the nature of the satellite lines is identified as monopole transitions (shake-up) from the occupied MO's of XeF_2 to the antibonding and/or Rydberg-state orbitals. Our results demonstrate the considerable potential of using such a simple atomic model, along with the Xα–SW calculations, to interpret the shake-up spectra of molecules.

Computational Details

(a) SCF–Xα–SW Calculation. For the interpretation of the satellite levels observed in the ESCA spectra, it is essential to understand the electronic structure of the ground and excited states of XeF_2. Although the multiconfiguration interaction Hartree–Fock (HF) method can provide very accurate information on the bonding of molecules, it is not practical in the study of a very heavy molecule like XeF_2. The SCF–Xα–SW method is superior to the HF method in this respect. By use of Slater's "transition-state" concept,[9] quantitative agreement has been obtained between observed and calculated optical transition energies in many molecules. The detailed theory of this method has been thoroughly discussed by Johnson[10] in a recent review and will not be repeated here.

SCF–Xα–SW calculations were carried out on the ground-state and 3d hole state electronic configuration of XeF_2. XeF_2 was assumed to be linear having a Xe–F distance of 2.00 Å.[5] Schwarz's α_{HF}[11] values were used for the atomic-exchange parameters. For the extramolecular and intersphere regions, a weighted average of the values used in the atomic region was used. The weighting factors are proportional to the number of valence electrons in the respective neutral atoms. Norman's nonempirical procedure[12] was used to obtain the ratio of sphere radii, which were chosen so that the spheres overlap by 10%.[13] The highest l values used in the basic functions are 3, 3, and 2 for the outer, xenon, and fluorine spheres. The sphere sizes and exchange parameters used in the calculation are given in Table I. The initial molecular potential was constructed by superposition of electron density of neutral Xe and F atoms. $D_{\infty h}$ symmetry was used to simplify the secular matrix. Core levels were never frozen during the iterations. The convergence criteria used required that the difference in the constant potential between successive cycles be less than 0.001 Ry.

Table I. Parameters Used in the Xα–SW Calculation (au)

region	X	Y	Z	R	α
Xe	0.0	0.0	0.0	2.4447	0.69984
F	0.0	0.0	3.7795	1.7128	0.73732
F	0.0	0.0	−3.7795	1.7128	0.73732
outer	0.0	0.0	0.0	5.4922	0.72369

Table II. Experimental Term Values for the Rydberg-State Orbitals for Xe, XeF_2, and XeF_4 (eV)

orbital	Xe[a]	XeF_2[b]	XeF_4[b]
6s	−3.77 (−3.90)	−3.75	−3.7
6pπ	−2.40	−2.75	−2.5
6pσ	−2.40	−2.45	−2.2
5d(δ)	−2.06	(−2.25)	−1.85(−2.15)
5d(π)	−2.05		
7s	−1.56 (−1.56)	−1.7	−1.6
7pπ		−1.4	−1.3
7pσ		−1.2	−1.2
6d(δ)	−0.96	(−1.15)	−0.95
8s	−0.86	−0.9	−0.9

[a] C. E. Moore, Atomic Energy Levels, *Nat. Bur. Stand.* (*U.S.*), *Circ.*, No. 467 (1958). [b] U. Nielsen and W. H. E. Schwarz, *Chem. Phys.*, 13, 195 (1976).

(b) Empirical Atomic Model. In an interesting series of papers, Lindholm[14] explored the behavior of the Rydberg term values for diatomic molecules. He demonstrated that the term value is independent of the "nature of the molecule" and the originating MO. The term value of the Rydberg-state orbitals is only dependent on the potential of the ionic core state. Extending Lindholm's idea to larger systems, one would expect that the Rydberg term values of Xe in atomic Xe and XeF_2 will be very similar. The excellent experimental work on the electronic spectra of gaseous Xe,[15] XeF_2,[3b] and XeF_4[3b] has confirmed this expectation. We can calculate the term values of the Rydberg state orbitals by fitting the UV electronic-transition energies into a Rydberg series. The term values of several Rydberg-state orbitals of Xe, XeF_2, and XeF_4 are tabulated in Table II. The maximum difference in the term values of each Rydberg-state orbital in different molecules does

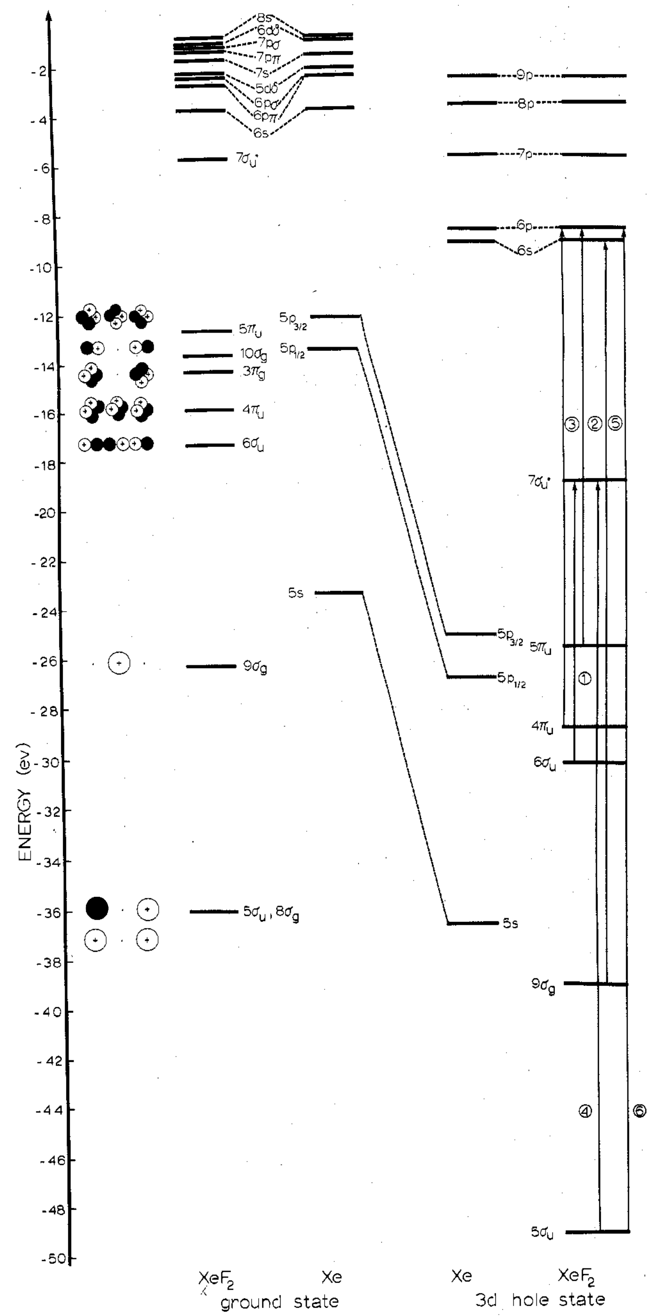

Figure 1. Molecular orbital diagram of Xe and XeF_2 at the ground state and 3d core hole state.

not exceed 0.2 eV. This strongly indicates dominant Xe Rydberg character in the unoccupied molecular orbitals of XeF_2 and XeF_4.

The binding energies of the filled valence orbitals in Xe[8] and XeF_2[4] can be obtained from high-resolution ESCA. The energies of the unoccupied molecular orbitals have been obtained from the term values determined from the UV absorption spectra. The $7\sigma_u$* molecular orbital is positioned by using the first intense $10\sigma_g \rightarrow 7\sigma_u$* absorption band at 7.85 eV. A ground-state MO diagram for Xe and XeF_2 is reconstructed in Figure 1 from the above UV and ESCA data. The most striking similarity between Xe and XeF_2 MO diagrams is the extremely similar energies of the unoccupied virtual orbitals in both molecules (Table II). Another feature of the MO diagram is the substantial shift of the 5p orbital energies due to chemical bonding.

In order to construct an MO diagram for the 3d core-ionized XeF_2 (Figure 1, right), we use the 3d shake-up spectrum of Xe gas[8] along with an extension of Lindholm's ideas.[14] From the Xe shake-up spectrum, the shake-off limit of Xe $5p_{3/2}$ in Xe is estimated at about 25.1 eV. The shake-up transition energy for $5p_{3/2} \rightarrow 6p_{3/2}$ is at 16.47 eV. We then calculate the term value of the $6p_{3/2}$ orbital as −8.6 eV. The higher Xe gas Rydberg-term *p* values are obtained in the same way. The 6s orbital energy is set by the 5s → 6s shake-up peak at 26.96 eV[8] in Xe gas. Since the $9\sigma_g$ orbital (85% Xe 5s character[5b]) is chemically shifted by 2.88 eV, the $9\sigma_g \rightarrow$ 6s shake-up is calculated at 29.84 eV. We then assume that the Rydberg-state orbitals in 3d core-ionized XeF_2 are principally Xe in character and that their term values are the same as those in Xe gas. We further assume that the MO's in XeF_2 will shift the same amount as the Xe atom 5p orbitals after 3d ionization. The $5p_{3/2}$ state in Xe gas drops by ca. 13.0 eV in the 3d ionized state, and we thus lower the XeF_2 MO's by the same amount.

This latter assumption appears to be crude—especially for those orbitals which are not of majority Xe 5p character. However, our SCF–Xα calculations (Table IV) give a shift of very close to 8.3 eV for all the $7\sigma_u$*, $5\pi_u$, $4\pi_u$, and $6\sigma_u$ orbitals having substantial Xe 5p character and no less than 7.5 eV for the other MO's. All of these shifts are slightly smaller than the calculated Xe 5p shift in Xe gas between the ground state and 3d core hole state of 10.2 eV[16] (compared to the observed value of 13.0 eV). Our assumption then should lead, if anything, to an overestimate of the shake-up energies by about 2–3 eV.

Experimental Section

Spectra were obtained on a McPherson 36 photoelectron spectrometer by using Al Kα X-rays. XeF_2 crystals were prepared by a previously reported method[17] and used without further purification. The gas pressure in our gas cell, although not measured directly, is not high enough to observe satellites due to inelastic scattering. For example, our shake-up spectra of CH_4[18] do not show the inelastic peak and shoulder at 9.9 and 15 eV, respectively, seen by Pireaux et al.[19]

Decomposition of XeF_2[4] was minimal, as evidenced by the absence of the Xe gas peaks. The spectra were fit by a least-squares program written by Coatsworth[20] and modified to constrain spin–orbit doublets by R. P. Gupta. Each peak is fitted to an analytical function which is a sum of Gauss–Lorenz shape functions. The positions of the satellite peaks were calculated by a "best-fit" criterion by using the spin–orbit splitting and intensity-ratio parameters obtained from first fitting the 3d and 4d doublets. The 4d spectrum was fitted by using satellite line positions obtained in the 3d spectrum and by fixing the spin–orbit coupling constant to that of the main 4d photolines. The intensities of the peaks were allowed to vary in a fashion similar to that observed in the 3d spectrum. We should emphasize that these spectra were computed before our theoretical studies began.

Results and Discussion

(a) Electronic Structure of XeF_2 in Ground and Hole States. The electronic distribution in various atomic spheres and the ionization potential of the valence molecular orbitals of XeF_2 were calculated by using an SCF transition-state potential with a half electron removed from the $5\pi_u$ molecular orbital. The ordering of the valence levels is $5\pi_u < 10\sigma_g < 3\pi_g < 4\pi_u$. The calculated ionization energies and intensities ratios are given in Tables III and IV. The Xα–SW calculation puts the antibonding $5\pi_u$ orbital above the nonbonding $10\sigma_g$, in contrast to the earlier ab initio SCF MO calculation.[5b] Our calculation, however, is in complete agreement with a DV–Xα calculation[6] and the experimental assignments.[4,5a] The agreement between the calculated and observed ionization energies is very pleasing. Also, we have calculated some UV-absorption transition energies by using Slater's transition-state procedure.[9] Calculated (and observed[3b]) transition energies (eV) usually agree to within ~1 eV, as is illustrated by the energies for the lowest two transitions: $5\pi_u \rightarrow 7\sigma_u$*, 4.71 eV (5.4 eV); $10\sigma_g \rightarrow 7\sigma_u$*, 6.32 eV (7.85 eV). Even better agreement is found for

Table III. Experimental and Theoretical Binding Energies (eV) and Intensities for Valence Molecular Orbitals for XeF_2

		theor[b]	
orbital	exptl[4]	this work[a]	ref 5b
$5\pi_u$	12.65	13.31 (1)	12.51 (1)
$10\sigma_g$	13.62	14.42 (0.15)	11.79 (0.17)
$3\pi_g$	14.33	15.50 (0.20)	14.71 (0.20)
$4\pi_u$	15.87	15.72 (0.67)	15.92 (0.74)
$6\sigma_u$	17.39	18.07 (0.38)	16.93 (0.34)
$9\sigma_g$	26.28	25.19 (0.86)	25.24 (1.0)
$5\sigma_u$	36.23	33.88 (1.13)	37.10 (2.7)
$8\sigma_g$		33.96 (1.14)	37.20

[a] Calculated from the transition potential of $5\pi_u$ orbital. [b] Intensity ratios in parentheses.

transitions to the Rydberg orbitals. The theoretical photoelectron intensities have been calculated with the intensity model.[21] In this model, the intensity of the jth molecular orbital I_j^{MO} is proportional to

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

on the assumption of 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 Aλ orbital, $\beta_{A\lambda}^{AO}$ is the corresponding atomic asymmetry parameter, and $(P_A^{AO})_j$ is the "probability" of finding the jth molecular orbital containing an electron belonging to the atomic Aλ orbital. In the context of the Xα–SW method, we estimate $(P_{A\lambda}^{AO})_j$ as the percentage of the charge in the respective atomic sphere plus the contribution of charges in the intersphere region. Partition of the intersphere charges into atomic spheres is proportional to the ratio of the valence electrons of the atomic sphere. We have calculated the relative I_j^{MO} values by using the $(P_{A\lambda}^{AO})_j$ values from the Xα–SW calculation and the $\sigma_{A\lambda}^{AO}$ and $\beta_{A\lambda}^{AO}$ values given by Scofield,[22] Nefedov et al.,[21c] and Kennedy and Manson.[23] The agreement again is excellent as compared with previous calculations and experiments.[4]

The overall bonding scheme of XeF_2 is very simple. The $5\sigma_u$ and $8\sigma_g$ are majority F 2s. The $9\sigma_g$ is mainly Xe 5s. The only bonding levels are $6\sigma_u$ and $4\pi_u$ derived from the Xe 5p and F 2p orbitals. The $3\pi_g$ and $10\sigma_g$ are fluorine nonbonding p orbitals, and finally $5\pi_u$ has a strongly XeF antibonding character. The $7\sigma_u$* orbital is the only low-lying σ* orbital corresponding to $6\sigma_u$. Other virtual orbitals of higher energy are diffuse Rydberg-like orbitals, as can be judged by the concentration of charge in the outer-sphere region.

The core hole state of XeF_2 was generated by removing one electron from the 3d level. The resulting orbital energies and electron distributions are shown in Table IV. The most prominent change from the ground state to the core hole state is the contraction of outer-sphere electron density toward the intersphere region for the Rydberg-state orbitals. The bonding orbitals of σ symmetry have a relatively small change, but there is an increase of charge in the Xe sphere for the π-bonding orbitals, as the π electrons are less bound in the ground state of XeF_2. The energy shift of the virtual orbitals and bonding orbital is significant. More Rydberg-state orbitals were found in the core hole state of XeF_2 since the change of potential of the ionic core causes Rydberg-state orbitals near the continuum to be more bounded. The approximate character of the orbitals can be identified by the partial wave components in the constituent spheres. One also observes in Table IV that the binding-energy shift of the occupied molecular orbitals is usually larger than the unoccupied molecular orbitals. As noted above, it is interesting to note that $6\sigma_u$, $4\pi_u$, and $5\pi_u$ and the antibonding $7\sigma_u$* orbitals, which have substantial Xe 5p character, shift almost uniformly by ~0.6 Ry (~8.5 eV). From these calculations and the MO diagrams in Figure 1, it is apparent that assignment of shake-up transitions by using ground-state MO calculations and UV energies may well lead to erroneous results due to a large shift of molecular orbitals and Rydberg orbitals from the ground state to core hole state.

(b) Shake-up Satellite Structure in XeF_2. Satellite lines observed on the high-binding-energy side of the main photoline can originate in a number of ways.[24] The most probable explanation for the satellite lines is shake-up.[25] As mentioned

Table IV. Calculated Eigenvalues (Ry) and Charge Distribution (%) for XeF_2 Ground State and 3d Hole State Valence Molecular Orbitals[a-c]

	ground state					hole state				
sym	energy, Ry	outer, %	Xe, %	F, %	inter, %	energy, Ry	outer, %	Xe, %	F, %	inter, %
$8\sigma_g$	−2.49597	0.42	5.74, s	87.26, s	6.58	−3.05750	0.33	9.93, s	83.50, s	6.24
$9\sigma_g$	−1.85096	0.16	77.27, s	11.47, s	11.10	−2.59500	0.13	78.40, s	13.25, s	8.22
$10\sigma_g$	−1.05973	1.56	10.94, s, d	76.63, p	7.87	−1.62871	1.20	9.73, s, d	82.37, p	6.69
$11\sigma_g$*	−0.30053	34.90, s	3.61, s	0.76, p, d	60.73	−0.69565	24.10	4.86, s	0.81, p, d	70.23
$12\sigma_g$*	−0.17084	30.57, d	8.91, d	0.14, d	60.39	−0.60513	12.99	22.72, d	0.16, d	64.12
$13\sigma_g$*						−0.31059	64.48, s	5.83, d	3.35, s	26.35
$14\sigma_g$*						−0.22367	90.06, s	1.19, s	0.66, s	8.08
$3\pi_g$	−1.10235	0.51	0.89, d	84.10, p	14.50	−1.64074	0.34	0.95, d	85.87, p	12.84
$4\pi_g$*	−0.09672	44.62, d	5.76, d	2.31, p	45.32	−0.52633	13.18	23.86, d	5.638, p	57.32
$5\pi_g$*						−0.24192	67.12, d	17.92, d	0.87, d	14.09
$5\sigma_u$	−2.48991	0.56	3.31, p	90.11, s	6.02	−3.01486	0.47	8.87, p	90.10, s	5.59
$6\sigma_u$	−1.32798	1.34	32.35, p	57.56, p	8.75	−1.94624	0.88	43.45, p	47.76, p	7.91
$7\sigma_u$*	−0.62932	1.99, p	47.05, p	36.93, p	14.04	−1.28768	1.21	42.83, p	47.54, p	8.42
$8\sigma_u$	−0.12740	59.89, p	3.76, p	2.26, p, d	34.09	−0.50337	31.65, p	14.31, f	2.95, p, d	51.09
$9\sigma_u$*						−0.45077	2.34, f	81.46, f	0.22, d	15.97
$10\sigma_u$*						−0.35558	16.83, p	74.47, f	3.45, s	5.24
$11\sigma_u$*						−0.21116	63.01, f	8.97, f	0.26, f	27.75
$12\sigma_u$*						−0.19228	88.38, p	3.98, p	0.41, p	7.23
$4\pi_u$	−1.15532	0.60	25.01 p	54.13 p	20.25	−1.77683	0.17, p	62.21, p	18.10, p	19.52
$5\pi_u$	−0.97530	0.34	43.62 p	32.07 p	18.97	−1.59222	0.41	18.97, p	69.38, p	11.23
$6\pi_u$*	−0.18641	51.24 p	5.13 p	0.47 p	43.15	−0.56584	35.09	5.62, p	0.44, p	58.84
$7\pi_u$*						−0.44836	2.18, p	82.40, f	20.0	15.40
$8\pi_u$*						−0.42113	1.10, p	88.46, f	2.35, p	8.09
$9\pi_u$*						−0.20832	64.63, f	8.14, f	0.0	2.72
$10\pi_u$*						−0.19739, p	91.84, p	0.96, p	0.04	7.16
$11\pi_u$*						−0.17339, p	83.60, f	0.08, f	1.40	14.19

[a] Calculated by using the transition state potential of $5\pi_u$. [b] Outer and inter represent the percentage charge of the outer-sphere and intersphere region. [c] Spherical-harmonic basis functions contributing more than 50% within the atomic sphere.

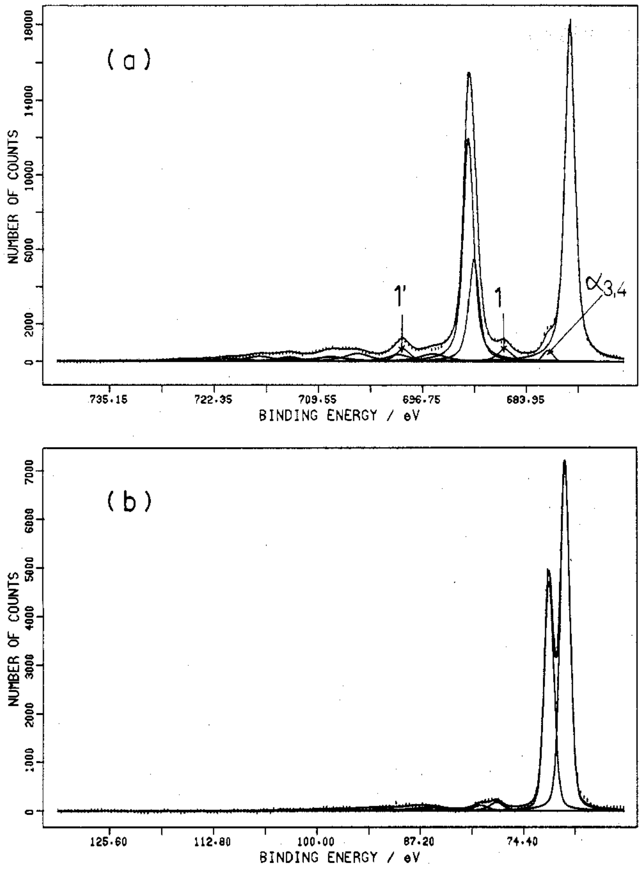

Figure 2. Al Kα photoelectron spectrum of XeF$_2$: (a) 3d core hole, (b) 4d core hole.

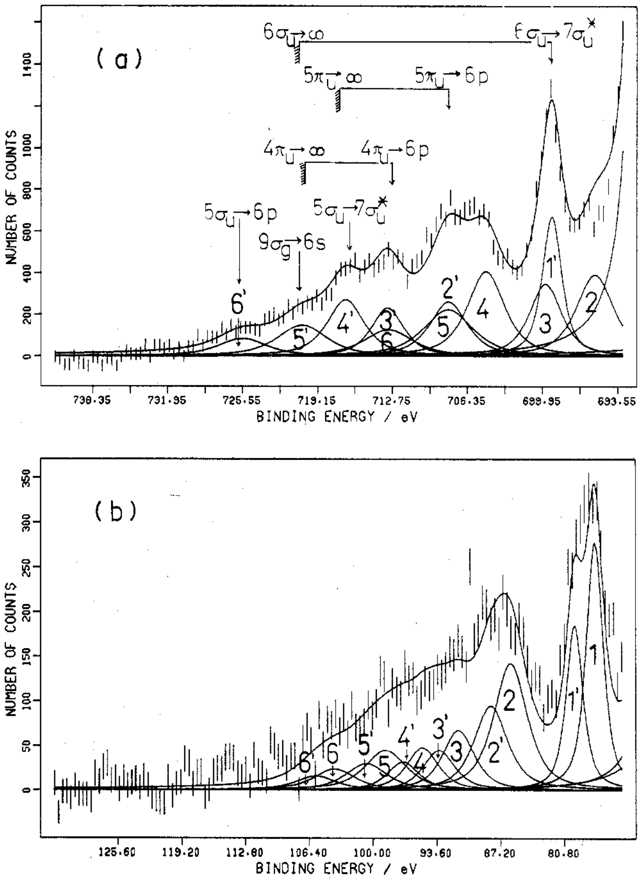

Figure 3. Shake-up spectrum of XeF$_2$: (a) 3d core hole, (b) 4d core hole.

previously, inelastic scattering has not been found in other molecules in our instrument and seems very unlikely here. Multiplet splitting is not possible because the ground state of XeF$_2$ is diamagnetic with a totally symmetric $^1\Sigma_g$ ground state.

In a shake-up process, the energy of the photoelectron leaving the molecule is "shared" with valence electrons, and a valence electron is promoted to an excited state. In order to preserve the simplicity of the one-electron model, we interpret the shake-up satellites in the context of the sudden approximation.[26] Under the sudden approximation, the probability, P, of a particular shake-up satellite occurring is[24,27]

$$P = |\langle \psi_f | \psi_i \rangle|^2$$

where ψ_i and ψ_f are the wave functions describing the molecular system before and after photoionization. On the basis of this simple one-electron overlap model, we expect, first, that for nonvanishing P, $\Gamma(\psi_f) \times \Gamma(\psi_i)$ must contain the A$_1$ representation. This leads to the monopole selection rule—the symmetry-allowed electronic excitations are between molecular orbitals of the same symmetry type. Second, the magnitude of P depends on the extent of overlap between the initial- and final-state wave functions. Hence, for intense shake-up, we expect that the initial- and final-state wave functions should have similar spatial distributions.[24] Also, simple two-configuration models[28] have shown that the intensity of the shake-up satellite line should be inversely proportional to the separation energy from the main photoline. For example, in Xe gas, the shake-up intensity decreases as the quantum number of the Rydberg-state orbitals increases.[8]

The Xe shake-up spectrum is most readily observed on the intense Xe 3d photolines.[22] However, the F 1s line strongly overlaps the Xe 3d$_{3/2}$ line (Figure 2), and F 1s shake-up could contribute to the overall shake-up spectrum (Figure 3). For the following three reasons, F 1s shake-up should not give an important contribution to the 3d shake-up spectrum. First, the F 1s primary line is one-third the height of the Xe 3d$_{3/2}$ line[4] and is less than one-fourth the height of the 3d$_{5/2}$ line. Second, by use of the same shake-up positions as in the Xe 3d spectrum, the Xe 4d spectrum is consistent with the Xe 3d spectrum (Figure 3). Third, most of the possible shake-up transitions are to Xe Rydberg orbitals. Since we do not expect intense shake-up if the initial and final states occupy different regions in space, shake-up involving the Xe Rydberg levels should be much more intense on Xe than on F levels. However, because the $7\sigma_g^*$ orbital has appreciable F character (Table IV), we would expect to see shake-up corresponding to the transitions $10\sigma_g \to 7\sigma_u^*$ (under $C_{\infty v}$ symmetry, both σ_u and σ_g symmetries transform as σ^*) and/or $6\sigma_u \to 7\sigma_u^*$ of comparable relative intensity to that of the Xe 3d shake-up. Thus there could well be a F 1s shake-up peak in the region of peaks 1' and 3 (Figure 3a) of about one-third the intensity of peak 1'. Indeed, peak 1' is too large relative to 1 (Figure 2) based on the normal spin–orbit intensity ratio of ~1:1.4.

The satellites in Figures 2 and 3 can thus be associated with Xe, and this shake-up must originate mostly from filled MO's with appreciable Xe character—the $9\sigma_g$, $6\sigma_u$, $4\pi_u$, and $5\pi_u$ MO's with large Xe 5p and 5s character. Shake-up transitions from the $8\sigma_g$, $5\sigma_u$, $3\pi_u$, and $10\sigma_g$ MO's of largely F character are considered less likely on this basis.

From the above considerations, and the MO diagram in Figure 1, we can readily assign most of the shake-up peaks in Figures 2 and 3 (see also Table V). We consider only transitions to the first member of the Rydberg series (i.e., 6s or 6p), because the intensity of the transition to higher members of the Rydberg series has been found to be much weaker (<20%, Figure 18, ref 8). Both the atomic model and Xα calculations predict the same order, and both calculations give reasonable agreement with experiment. As might be

Table V. XeF_2 3d Core Level Satellite Lines

		energy, eV				
line no.	assignt	obsd	3d-fwhm (intens[a])	4d-fwhm (intens[b])	atomic model	Xα-SW[c]
1	$6\sigma_u \rightarrow 7\sigma_u{}^*$	8.05 ± 0.2	2.0 (7.5)	2.0 (4)	11.6	9.03
2,2′	$5\pi_u \rightarrow 6p\ (6\pi_u{}^*)$	16.9 ± 1.0	3.8 (5.6)	4.0 (3.4)	17.00	13.48
	$5\pi_u \rightarrow 7p\ (7\pi_u{}^*)$					16.13
	$5\pi_u \rightarrow 8p\ (8\pi_u{}^*)$					16.76
	$5\pi_u \rightarrow 9p\ (10\pi_u{}^*)$					18.02
3,3′	$4\pi_u \rightarrow 6p\ (6\pi_u{}^*)$	22.1 ± 0.5	3.3 (4.3)	3.8 (1.7)	19.61	18.43
	$6\sigma_u \rightarrow 6p\ (8\sigma_u{}^*)$				21.73	19.05
4,4′	$5\sigma_u \rightarrow 7\sigma_u{}^*$	25.7 ± 0.5	3.8 (5.8)	3.8 (.74)	30.40	23.07
5,5′	$9\sigma_g \rightarrow 6s\ (11\sigma_g{}^*)$	29.4 ± 1.5	5.0 (4.2)	5.0 (.88)	29.84	26.51
6,6′	$5\sigma_g \rightarrow 6p\ (8\sigma_u{}^*)$	34.5 ± 1.5	5.0 (2.4)	5.0 (.44)	40.57	34.50

[a] In percent, relative to the main photoline at 678.62 eV. [b] In percent, relative to the main photoline at 69.26 eV. [c] Calculated by using transition-state approach.

Table VI. Effective Quantum Number of Xe Calculated from Electronic and Shake-up Transitions

electron transition, eV					shake-up transition (3d hole state), eV				
transition	energy	term value	n^*	Δn^*	transition	energy	term value	n^*	Δn^*
$4d_{3/2} \rightarrow 6p_{3/2}$	67.02	−2.48	2.34		$5p_{3/2} \rightarrow 6p_{3/2}$	16.47	−8.63	2.51	
$\rightarrow 7p_{3/2}$	68.29	−1.19	3.38	1.04	$\rightarrow 7p_{3/2}$	19.44	−5.66	3.10	0.59
$\rightarrow 8p_{3/2}$	68.78	−0.70	4.42	1.03	$\rightarrow 8p_{3/2}$	21.50	−3.60	3.89	0.78
$\rightarrow 9p_{3/2}$	69.09	−0.39	5.92	1.50	$\rightarrow 9p_{3/2}$	22.60	−2.50	4.66	0.77
$\rightarrow \epsilon p_{3/2}$	69.48				$\rightarrow \epsilon p_{3/2}$	25.1			
δ^a (av)			3.49					3.96	

[a] Values obtained by fitting $T = -Z^2/(n-\delta)^2$ Ry.

expected, the best agreement between experiment and the atomic model is obtained for the shake-up (2 and 2′) involving the $5\pi_u$ orbital of very high Xe 5p character. The calculated $5\pi_u \rightarrow 6\pi_u{}^*$ ($6p_\pi$) energy is 17.00 eV, in excellent agreement with the observed value of 16.9 eV. Similarly, the predicted (29.84 eV) and observed (29.4 eV) shake-up energies for the shake-up (5 and 5′) involving the $9\sigma_g$ orbital of mainly Xe 5s character are in very good agreement. The assignments for lines 1,1′ and 3,3′ are also relatively straightforward, and the agreement between predicted and observed values is reasonable. Difficulties arise with lines 4,4′ and 6,6′. No calculated transitions from MO's having appreciable Xe 5s or 5p character fall in this energy range. We suggest a very tentative assignment—4 and 4′ to $5\sigma_u \rightarrow 7\sigma_u{}^*$ and 6 and 6′ to $5\sigma_u \rightarrow 8\sigma_u{}^*$ (6p). This assignment gives reasonable agreement between observed and predicted energies. If we look at the symmetry of the $5\sigma_u$ orbital wave function, it is very much like a diffuse Xe p orbital. For example, by comparing the $5\sigma_u$ orbital with the 6p orbital ($8\sigma_u{}^*$), we observe that the electrons in these two MO's occupy the same region of space. The overlap between the $5\sigma_u$, $7\sigma_u{}^*$, and $8\sigma_u{}^*$ orbitals should be nonnegligible and may give rise to the two shake-up pairs, 4,4′ and 6,6′.

Looking at the Xα-SW-calculated shake-up energies, we find that, with the exception of the first shake-up peak, the method always underestimates the shake-up transition energy.[29] This effect is probably due to the unsatisfactory potential used for the Rydberg-state orbitals in the Xα method. The long-range behavior of the Rydberg-orbital potentials is no longer Coulombic.[30] Finally, it is interesting to look at the line widths of the satellite lines. All the satellite lines are considerably broader than the main photoline. Generally, the line width increases and the intensity decreases as the shake-up energy increases. Some of the shake-up peaks could be an overlap of two or more peaks due to spin–spin and spin–orbit states. For example, weak satellites in the C 1s spectra of $Cr(CO)_6$[7] have recently been attributed to spin–spin coupling by using an ab initio SCF CI calculation.[31] Because the binding energy of the Xe 3d level is so large (~680 eV), we expect that the overlap and the resulting exchange integrals between the valence orbitals and the core hole will be very small. We should be approaching the limit of weak coupling, when there will be only one strong peak due to the final-state valence singlet.[32] Also, lines 4,4′, 5,5′, and 6,6′ are relatively near the double ionization (shake-off) limit of $4\pi_u$ and $5\pi_u$, and large line widths are then not unexpected.

(c) Suggestion for Future Work. In a series of papers in the study of molecular Rydberg states between molecules and atoms, McGlynn et al.[33] attempted to apply the phase-amplitude method from scattering theory[34] to extract information on the residual, atomic, and molecular potentials.

The effective quantum number n^* of a term value is related to the principal quantum number n and the quantum defect δ as[35]

$$n^* = n - \delta$$

and since δ is a measure of the phase shift of the wave function induced by the change in the core potential,[36] the variation of n^* will provide us with some details of the molecular potential. McGlynn has shown that if the change in n^* (Δn^*) between two successive Rydberg-state orbitals is greater than or equal to 1, the residual potential is attractive. Otherwise, it is repulsive.[33] Therefore, the behavior of the effective quantum number should contain information about the residual potential. The knowledge of the residual potential should be important in the study of relaxation effects.

In Table VI we have calculated the effective quantum number of the gaseous Xe 5p series, from the shake-up transition energy of Gelius,[8] and compared the effective quantum number obtained from the $4d_{3/2} \rightarrow np_{3/2}$ electronic transition.[37] The Xe gas shake-up transitions closely resemble a doubly ionized state, whereas the electronic transition resembles a singly ionized cationic state. The quantum defects are calculated by fitting the Rydberg p series. As expected intuitively, the quantum defect from the Xe-shake-up Rydberg series is larger than for the Xe-optical transition Rydberg series. In a doubly ionized state, the virtual Rydberg-state orbitals will be more bound than the singly ionized states. It is also interesting to compare the difference in effective quantum numbers for the two states of Xe. For the Xe singly ionized state, the residual potential is always attractive. In the case of Xe shake-up, the Δn^* values indicate that the residual potential is repulsive.

We would like to be able to apply these ideas to molecules such as XeF_2 in which most of the transitions are atomic-like. Unfortunately, the resolution of the shake-up spectrum is not good enough to allow us to make such a calculation. In the future, it may be possible to obtain much higher resolution with synchrotron radiation.[38]

Conclusions

In the relatively simple large molecule XeF_2, we have been rather successful in using a simple atomic model and Xα calculation to assign the shake-up spectrum. This atomic model should be very useful in the future for assignment of shake-up spectra of molecules.

While the shake-up spectra are complementary to optical spectra, there are several advantages of the shake-up method for obtaining information on antibonding and virtual levels. We can measure shake-up transitions up to ~40 eV without difficulties, while electronic transition energies are normally measured up to a few eV with conventional radiation sources. Especially when higher resolution is obtained, a shake-up spectrum may well be simpler than an optical spectrum because there will be fewer allowed monopole than dipole transitions. Molecular orbital information from the shake-up spectrum will certainly aid the optical assignments. For example, in XeF_2, the $7\sigma_u{}^*$ orbital (of substantial Xe 5p character) shifts more than the other Rydberg levels in the hole state. This relaxation shift should be useful in distinguishing antibonding valence orbitals from Rydberg orbitals. Along this same line, it is important to realize that we can usually obtain shake-up spectra on different atoms in the same molecule.[7] The relaxation shift of an MO or Rydberg level will depend on the position of the hole in the molecule. Profound differences in the shake-up energy in different atoms of the same molecule may well be an important guide in characterizing MO's of that molecule.

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