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Auger energy shifts and core level relaxation energies in XeF_2, XeF_4, and XeF_6

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The energy shifts in $3d$ photoelectron and $M_4N_{4,5}N_{4,5}$ Auger spectra of Xe have been studied for XeF_2, XeF_4, and XeF_6 molecules in the gas phase. Using the Auger parameter method, the contributions of the initial state chemical and final state extra-atomic relaxation effects to the observed shifts have been estimated. The relaxation part has found to be significant both in the binding energy (up to 1.8 eV for XeF_6) and especially in the Auger shifts. The ground state shifts are thus larger than the $3d$ binding energy shifts reported earlier. Calculated atomic charges are also now in better agreeement with theory and other experimental values.

I. INTRODUCTION

The Xe $3d$ and $4d$ binding energy shifts in the xenon fluorides XeF_2, XeF_4, and XeF_6 have been studied by several authors.[1-3] The Xe $3d$ chemical shifts referred to atomic xenon are very large, ranging from 2.9 to 7.8 eV on going from XeF_2 to XeF_6. Using the point charge model, and assuming that the relaxation energies are the same for all molecules studied, Carroll et al.[2] calculated atomic charges on the Xe and F for these molecules. Somewhat surprisingly, they found that the charge per fluorine is -0.24 e regardless of the compound—considerably smaller than theoretical and other experimental values.

In this paper, we present the experimental $M_4N_{4,5}N_{4,5}$ Auger energies for the three xenon fluorides. The Auger shifts are very different than the $3d$ binding energy shifts due to relaxation effects. Using the Auger parameter method, estimates of the initial-state chemical shift and the final-state extra-atomic relaxation contributions to both shifts have been obtained. The relaxation energies are rather large and not constant, and lead to different atomic charges than those calculated by Carroll et al.,[2] in better agreement with theoretical and other experimental values.

Because there have been rather few papers on the Auger shifts in inorganic molecules, it seems reasonable to review briefly the theory[4-8] to obtain relaxation energies. The binding energy of a core electron i can be written

$$E_B(i) = V(i) - R(i), \tag{1}$$

where $V(i)/e$ is the potential at the core electron i and $R(i)$ is the electronic relaxation energy due to the response of the charge distribution to the creation of the core hole. Using the one and two electron binding energies for the initial and final states of the Auger process, the energies of the outgoing electrons can be given by

$$E_{Aug}(ijk;X) = E_B(i) - E_{BB}(jk;X), \tag{2}$$

where $E_{BB}(jk;X)$ is the energy needed to remove electrons j and k for the specific $X = {}^{2S+1}L_J$ state. The double hole ionization energy can be written with the aid of single ionization energies [Eq. (1)] of electrons j and k and the Coulombic interaction energy $F(jk;X)$ between the two core holes. Thus

$$E_{Aug}(ijk; X) = V(i) - R(i)$$
$$- [V(j) + V(k) + F(jk;X) - RR(jk)], \tag{3}$$

where $RR(jk)$ is now the total relaxation energy for the double hole final state. The change in the Auger energy when the same atom is in different chemical environments is, assuming equal potential changes for different core orbitals of the atom and that the hole–hole interaction energy remains as a constant,

$$\Delta E_{Aug} = -\Delta V - \Delta R + \Delta RR. \tag{4}$$

The changes in the relaxation energies are mainly caused by the different extra-atomic relaxation energies and the atomic part can be usually considered as a constant. Within the linear polarization approximation, the extra-atomic relaxation or polarization energy is proportional to the square of the number of the created core holes, so $\Delta RR = 4\Delta R$. Thus the change of the Auger parameter α, which is the sum of the binding energy and the Auger energy, is

$$\Delta\alpha = \Delta E_B + \Delta E_{Aug} = 2\Delta R. \tag{5}$$

Obviously, a measurement of both Auger and binding energy shifts will give the relaxation contribution to both.

It should be noted that in this simplest form, this Auger parameter procedure is most valid for chemically similar compounds. Siegbahn and Goscinsky[9] and Thomas[6,7] have presented more accurate treatments of the Auger shifts. Taking the second order terms into account, Thomas[6,7] obtained the relation

$$\Delta\alpha = \Delta R - \frac{4}{3}\left[\frac{dk}{dN}\frac{dq}{dN}\right], \tag{6}$$

where N is the number of core electrons, q is the valence charge, and k gives the change in core ionization energy per electron removed from the valence shell. As pointed out by

Thomas,[6] the sign of the correction term in Eq. (6) is always positive. Thus the relaxation energies calculated from the uncorrected formula (5) represent upper limits. For the different xenon fluorides the correction term in Eq. (6) is assumed in the light of previous studies[1-3] to remain rather constant and thus at least the differences in the relaxation energies between different xenon fluorides calculated from the uncorrected formula are believed to be meaningful.

II. EXPERIMENTAL

The compounds were all synthesized by Schrobilgen using the referenced methods in Ref. 10. Both the $3d$ photoelectron and $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of XeF$_2$, XeF$_4$, and XeF$_6$ were taken with the McPherson 36 photoelectron spectrometer at the University of Western Ontario. The spectra were excited by Mg$K\alpha$ radiation, which bring the $3d$ photolines in the spectrum rather close ($\sim$40 eV) to the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra. The kinetic energy difference between the $3d_{5/2}$ photoline and the intense well-resolved $^1G_4, ^1D_2$ Auger line allows an accurate estimate of the Auger parameter.

The Auger spectra were fit by a least-squares program written by Coatsworth.[11]

III. RESULTS AND DISCUSSION

A. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra

The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra for Xe and XeF$_2$ are given in Fig. 1. The assignments of the components are taken from Ref. 12. At first sight, these spectra (and those of XeF$_4$ and XeF$_6$) look very similar to each other and also to published Xe Auger spectra.[12-14] All the major features in the XeF$_2$ spectrum (Fig. 1) are indeed similar to those of Xe. This is an expected result because the transitions take place between deep core levels. The $3d_{5/2}$ binding energies and the $^1G_4, ^1D_2$ Auger positions are quoted in Table I. In order to obtain these values the following procedure was used. The $3d_{5/2}$ binding energy value 676.70 eV given by Svensson *et al.*[15] was used as the reference energy. The binding energies for XeF$_2$ and XeF$_4$ were taken from Ref. 3, where the above given free atom value was used. The corresponding binding energy for XeF$_6$ was obtained using the experimental shift value between XeF$_4$ and XeF$_6$ reported by Carroll *et al.*[2] Their shift values agree well with those of Bancroft *et al.*,[3] but their $3d$ binding energy for Xe deviates from the value of Svensson *et al.*[15] The Auger energies are then readily obtained using the observed energy differences of Auger and
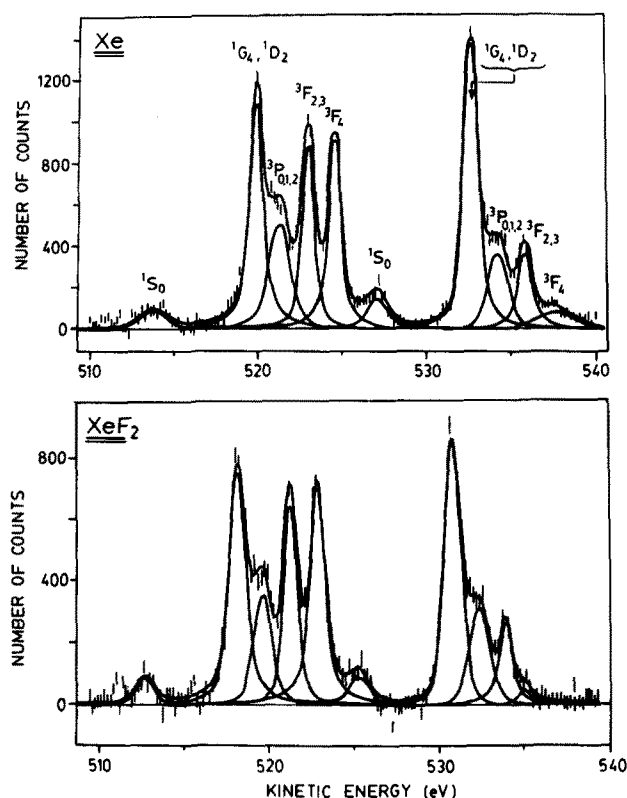

FIG. 1. $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectra of atomic Xe and XeF$_2$. The spectra were excited by Mg$K\alpha$ radiation. The assignments of the computer fitted line components are taken from Ref. 12.

photo peaks. The Auger energy for Xe atoms is taken from Ref. 16. The Auger and binding energy shifts are given in Table I. The Auger shift was also calculated from the centroid of the spectra, with identical results within the error.

In free Xe atoms the inherent widths for $3d$ and $4d$ levels are about 0.5 and 0.1 eV, respectively.[3] The accurate measurements of Bancroft *et al.*[3] using monochromatized Al$K\alpha$ radiation showed that the $3d$ and $4d$ photolines from XeF$_2$ and XeF$_4$ are slightly broader than from atomic Xe due to the ligand field splitting. In XeF$_2$, the $3d$ and $4d$ broadening was 0.05 and 0.12 eV, respectively, while the total widths were 0.92 and 0.76 eV, respectively. This analysis showed that the $3d_{3/2}$ level should split by 0.18 eV and $4d_{3/2}$ by 0.33 eV in XeF$_2$. The widths of the line components in our present Auger spectra are 0.9–1.1 eV for the main components. Therefore, a slight broadening of line components should appear between Xe and XeF$_2$. Careful inspec-

TABLE I. Experimental binding and Auger energies, and calculated relaxation energies and initial state shifts (in eV).

	$E_B(3d_{5/2})$	$\Delta E_B(3d_{5/2})$	$E_{Aug}(M_4N_{4,5}N_{4,5};^1G_4)$	ΔE_{Aug}	ΔR	ΔV
Xe	676.70[a]	...	532.68(15)[d]	...	...	...
XeF$_2$	679.63[b]	2.93	530.88(15)[e]	− 1.80	0.6	3.5
XeF$_4$	682.20[b]	5.50	529.62(15)[e]	− 3.06	1.2	6.7
XeF$_6$	684.43[c]	7.73	528.59(15)[e]	− 4.09	1.8	9.6

[a] Svensson *et al.* (Ref. 15).
[b] Bancroft *et al.* (Ref. 3).
[c] Obtained using ΔE_B (XeF$_4$–XeF$_6$) of Carroll *et al.* (Ref. 2).

[d] Aksela and Kumpula (Ref. 16).
[e] This work.

tion of component widths really shows indications of this. However the observed linewidths are clearly dominated by the lifetime broadening[12] of $3d$ and $4d$ levels and by the instrumental broadening. Also, the accurate determination of the linewidth broadening is difficult due to partly overlapping line components in the Auger spectrum. The sharpest line component is $^3F_4$ in the $M_4N_{4,5}N_{4,5}$ group in both spectra. This is the best separated single component. Its' width is found to be 0.15–0.2 eV broader in XeF₂ than in Xe. The most intense lines consist of two close lying $^1G_4$ and $^1D_2$ components whose separation is not accurately known (Fig. 1).

B. Energy shifts

Inspection of the shift values given in Table I shows that the binding energy shifts are exceptionally large for these molecules—up to around 8 eV. Within the simple Auger parameter model discussed above, the Auger energy shift without relaxation should be equally large but in the opposite direction. The values of Table I shows this general trend but the magnitudes are smaller, about half of the binding energy shifts. This clearly shows that the chemical initial state effects are dominating, but the relaxation effects have an essential contribution which increases with the number of F atoms in the compound.

Table I shows the ΔR values obtained from the changes in the Auger parameter. They range from 0.6 to 1.8 eV for a single core hole. It is interesting to note that the relaxation energies increase linearly with the number of F atoms around the ionized Xe atom (Fig. 2), in accordance with almost linear dependence both for the binding energy and Auger shifts. The linear dependence of ΔR is one more indication that the correction term in Eq. (6) is small.

The initial state potential shifts ΔV at the xenon site are then obtained as the sum of observed binding energy shifts and derived extra-atomic relaxation energies. They are given in Table I and Fig. 2. These quantities, rather than the bind-

ing energy shifts,[2] should then be compared to the potential energy changes of the Xe atom due to F atoms of the molecules.

Basch *et al.*[17] have carried out *ab initio* self-consistent field calculations for the xenon fluorides. Their results can be compared with ours using the extra-atomic relaxation energies corrected values. Their $4d$ binding energy shifts relative to atomic xenon are 4.20, 8.79, and 13.69 eV, for XeF₂, XeF₄, and XeF₆, respectively. The calculated values thus exceed our experimental values by 20%, 32%, and 43% for XeF₂, XeF₄, and XeF₆, respectively (Table I). The agreement is not very good but the correction using the relaxation energies makes a considerable improvement, and brings the experimental values on the right basis to be compared with calculations valid for the ground state in the neutral molecule before core ionization. As pointed out by Basch *et al.*,[17] this kind of single-configuration limited basis set MO calculations have a tendency to overestimate charge transfer among atoms in a molecule. This leads to too large binding energy shifts.

An alternative way to study these shifts can be based on the point charge model. The initial state chemical shift is given by

$$\Delta V = kq_i + \sum_{j \neq i} \frac{q_i}{r_{ij}}, \tag{7}$$

where the first term describes the interaction energy of the valence charge with the core level to be studied and the second term the potential change at the site of the atom caused by the valence charges q_j of the neighbor atoms at the interatomic distances R_{ij}. Using the above obtained ΔV values and the quoted[17] interatomic distances 2.00 (XeF₂), 1.95 (XeF₄), and 1.89 Å (XeF₆), it is then possible to calculate the valence charges q_{Xe} of Xe in each molecule if an estimate for k_{Xe} is available. The interaction constant k can be obtained from different semiempirical models[2] or *ab initio* atomic calculations using, e.g., the relativistic Dirac–Fock program.

We first calculate k in a very straightforward way from the change of the $3d$ core ionization potential when a $5p$ electron is removed from the xenon atom. Applying Grant's relativistic Dirac–Fock code,[18] the value of 10.8 V was obtained for k. Using this value, and the ΔV values obtained above (Table I), we calculate xenon valence charges $q_{Xe} = 0.97\ e$ in XeF₂, 1.97 e in XeF₄, and 3.00 e in XeF₆. Some authors state that k is equal to $e^2 \langle 1/r \rangle$, where r is the valence radius. For comparison, we have also calculated k using this definition and the same Dirac–Fock code. The result from the mean value of the $5p$ components was 15.2 V. This k value is thus clearly much larger and gives q_{Xe} values of 0.44, 0.86, and 1.26 e for XeF₂, XeF₄, and XeF₆, respectively.

Two important points arise from these results. First, the theoretically calculated k values deviate strongly and calculated valence charges are even more different. The latter k value leads to charges which are less than half of the former. Hence a reliable k value is of crucial importance to obtain reliable estimates for q's. Second, as previously noted by Carroll *et al.*,[2] the calculated Xe charges for both k values increase very linearly with the number of the fluorine atoms in
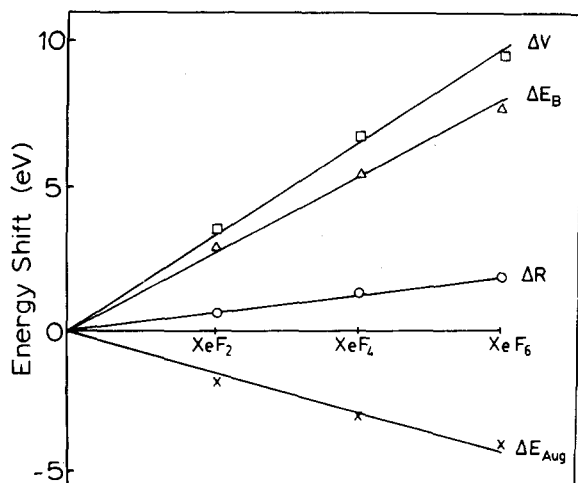

FIG. 2. Experimental binding energy shifts ΔE_B and Auger shifts ΔE_{Aug} for different xenon fluorides. From them we obtained the relaxation energy contributions ΔR and the initial state chemical shifts ΔV. Note the very closely linear dependence of all the quantities but especially of ΔR on the number of F atoms.

the molecule. Thus, the fluorine charge q_F is a constant for all compounds. This arises from the very linear increase of ΔV with the F atoms (Fig. 2) and very small changes in the interatomic distances.

This constant fluorine valence charge q_F in all three compounds for each k value provides a simplified method to solve for k_{Xe} from our experimental results for Xe. Actually we then have three equations with two unknown parameters k_{Xe} and q_F. The least square fit gives the $k_{Xe} = 11.8$ V and $q_F = -0.38\ e$. These values are much closer to those obtained using the binding energy change calculated k (10.8 V), and in reasonable agreement with the results of Carroll *et al.*[2] They obtained $k = 13.0$ V and also a constant $q_F = -0.24\ e$ from the set of uncorrected binding energy shift equations including also the fluorine 1s levels. Using their value of 13.0 V of k, we calculate $q_F = -0.3\ e$. The relaxation correction of the binding energies itself thus increases the resulting q values by 20% for constant k.

IV. CONCLUSIONS

We have determined the Xe 3d and MNN Auger extra-atomic relaxation energies for the xenon fluorides using the Auger parameter method. These relaxation energies are important, e.g., in comparing experimental and calculated binding energy shifts.

Using the corrected binding energy shifts, the intial state potential energy changes in the xenon compounds are readily obtained and a direct comparison with the point-charge model calculated values is possible. Applying the point-charge model, calculated valence charges per fluorine atom in these compounds are very accurately constant for a reasonable range of calculated k_{Xe} values. This provides the possibility to solve the parameter k for xenon and the valence charge per fluorine atom directly from experimental results. The obtained valence charge $q_F = -0.38\ e$ is considerably higher than the earlier result $-0.24\ e$ of Carroll *et al.*[2]

We have calculated theoretically the values of the parameter k both from the binding energy change when a valence electron is removed and from $e^2\langle 1/r\rangle$, where r is the valence radius. From the binding energy method, the k value of 10.8 V is much closer to the experimentally determined

value 11.8 V than from valence radius calculated 15.2 V. This indicates that the binding energy shift calculated k is a more reliable theoretical estimate.

However, it was found that the valence charges are very sensitive to the values of the k, and therefore reliable values of k are very important. Clearly, further experimental and theoretical work is needed in this area.

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