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Vibrational Broadening in F 1s Hole States and the $8a_{1g}$ Valence Orbital of XeF_6: Structure of XeF_6 and Heats of Formation of Unusual Cations

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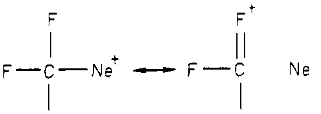
Abstract: We have recorded the F 1s X-ray photoelectron spectra of the rare gas fluorides (KrF_2, XeF_2, XeF_4, and XeF_6), the fluoromethanes (CH_3F, CF_3H, and CF_4), and HF. The large range of F 1s line widths for these and other fluorinated compounds (1.2 to 2.6 eV) is shown to be due to vibrational broadening. Using the equivalent cores approximation to quantify this broadening, we show that there is a rather good correlation between the dissociation energy for the reaction:

$$XNe^+ \rightarrow X^+ + Ne \ (X^+ = KrF^+, XeF^+, \text{etc.})$$

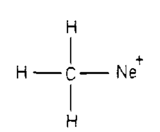
and the F 1s line width. Relative Lewis acidities toward Ne have been obtained from the dissociation energies or line widths, and heats of formation of the unusual cations (i.e., linear ClF_2^+ and T-shaped SF_3^+) are derived. The vibrational structure on the $8a_{1g}$ valence orbital of XeF_6 shows an average vibrational splitting of $\sim$530 cm^{-1}. This splitting is considerably smaller than the ground-state value and suggests that the $8a_{1g}$ orbital is bonding rather than antibonding as previously suggested. This vibrational analysis, our $X\alpha$ calculations, and the F 1s line width treatment all indicate that the very broad F 1s line width in XeF_6 is caused by vibrational broadening rather than inequivalent fluorines.

With the development of a monochromatized Al K_α X-ray source,[1] it became very evident that vibrational effects were responsible for considerable broadening in core level X-ray photoelectron or ESCA spectra. The C 1s spectrum of CH_4[1] clearly showed three peaks separated by $\sim$0.43 eV, which is close to the ground-state totally symmetric vibrational frequency (0.43 eV). In CO, the vibrational structure is not resolved on the C 1s level and simply gives rise to an asymmetric peak.[1] Theoretical interpretations of the half-widths vary from the equivalent cores technique[1] and Hartree–Fock model[2-6] to the more complex Green's function method.[7]

Different F 1s line widths were noted by Thomas[8] in the fluoromethanes. The peak widths for CF_4 and CH_3F (1.83 and 1.36 eV, respectively) are considerably broader than for F_2 (1.2 eV).[9] It was suggested for the first time[10] that this difference was the result of transitions to unbound states, and this was supported by the positive heats of formation of the equivalent core species. Jolly and Schaaf[11] have attempted a qualitative rationalization of different core line widths based on a combination of equivalent core and valence bond methods. The equivalent cores representation of the F 1s hole states in valence bond terms for CF_4 and CH_4 are as follows:



(1)



(2)

Some π bonding is present in CF_3Ne^+ that is not possible in CH_3Ne^+. The π bonding is expected to produce a strained configuration for the F 1s ionized species. This will produce a considerably different potential energy surface for the ion than for the neutral molecule and account for the difference in F 1s half-widths.

In an attempt to quantify this effect, Goscinski et al.[5] calculated the potential energy surfaces of CF_4 and CH_3F using an ab initio Hartree–Fock formalism. They assume that the vibrational excitation of a two-particle system consisting of CX_3 (X = H or F) and the F atom is the major factor responsible for the Franck–Condon profile of the spectra. Thus, the upper state is calculated as a function of the CX_3–F bond distance. In order to estimate the band envelope, the ground-state vibrational wave function is projected onto the upper state. It is then assumed that the upper state is an approximately local linear function. The following relation can be derived:[5]

$$\text{fwhm} = 2(\ln 2)^{1/2}\, m/\gamma^{1/2} \qquad (3)$$

where m is the slope of the upper state and γ is the exponent of the ground-state vibrational wave function. The calculated vibrational width ratio CF_4:CH_3F of 1.35 is in qualitative agreement with the experimental ratio of 1.75.

In this work we have developed a simple method for correlating vibrational broadening effects in F 1s hole states within the equivalent cores formalism. The method also provides a means of obtaining heats of formation of unusual cations and correlating the Lewis acidity of these cations toward neon. This work was motivated by the unusually broad F 1s line width in XeF_6. To characterize this broadening and to provide more information on the structure of XeF_6, we have also performed an $X\alpha$ calculation on XeF_6 and a high-resolution UV photoelectron study of the low binding energy $8a_{1g}$ orbital.

Experimental Section

The X-ray photoelectron spectra were obtained on our McPherson ESCA-36 photoelectron spectrometer using an Al K_α X-ray source. The Xe and Kr fluorides were prepared by Schrobilgen[12,13] by his referenced

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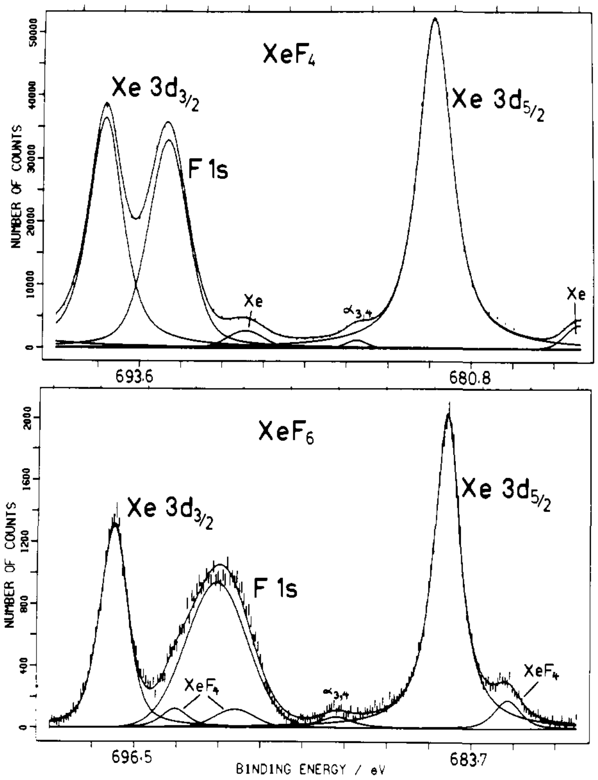

Figure 1. X-ray photoelectron spectra of the F 1s and Xe 3d orbitals in XeF_4 and XeF_6.

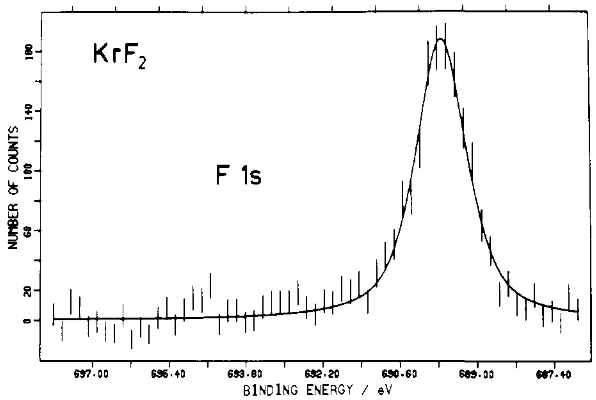

Figure 2. X-ray photoelectron spectra of the F 1s orbital in KrF_2.

methods. The fluoromethanes were commercially available Matheson research grade. Other F 1s widths for F_2, ClF_3, SF_4, and SF_6 were obtained from previous work.[9,14] Unstable compounds such as KrF_2 and XeF_6 were introduced into the spectrometer via a Kel-F line to minimize decomposition.[13] All binding energies were calibrated with respect to the F 1s level of HF at 694.0 eV,[15] which was confirmed in our study. The spectra were fitted by using a least-squares program described in previous papers.[12,13,16]

Results and Discussion

XeF_6 Structure. The incentive for this work stems from our spectra of the Xe and Kr fluorides[13] (Figures 1 and 2). We noted that the half-width of the F 1s level in XeF_6 (2.6 eV) was considerably broader than that in XeF_2 (1.50), XeF_4 (1.80), and KrF_2 (1.41 eV). We originally felt that the large enhancement in line width could be a result of inequivalent fluorines. Previous work on the structure of XeF_6[17-22] shows that it is definitely distorted from octahedral symmetry. The most recent analyses[18,20,22] describe the structure in terms of a mobile electron pair moving over the faces and edges of the octahedron and distorting it in a dynamic fashion. One of the more likely configurations would be that involving C_{3v} symmetry with the lone pair of electrons centered on a face of the octahedron.[17] The valence shell electron pair repulsion theory (VSEPR) then predicts that the three fluorines sharing the face with the lone pair should be pushed apart while the other three would be compressed.[23] Thus, a binding energy shift corresponding to the chemical inequivalence of the two sets of fluorines could account for the broadness of the F 1s peak in XeF_6.

Table I. XeF_6, Parameters Used in the Xα-SW Calculation (au)

region	*x*	*y*	*z*	*R*	α
Xe	0.0	0.0	0.0	2.1748	0.69984
F	3.5907	0.0	0.0	1.7754	0.73732
F	−3.5907	0.0	0.0	1.7754	0.73732
F	0.0	3.5907	0.0	1.7754	0.73732
F	0.0	−3.5907	0.0	1.7754	0.73732
F	0.0	0.0	3.5907	1.7754	0.73732
F	0.0	0.0	−3.5907	1.7754	0.73732
outer	0.0	0.0	0.0	5.3661	0.73132

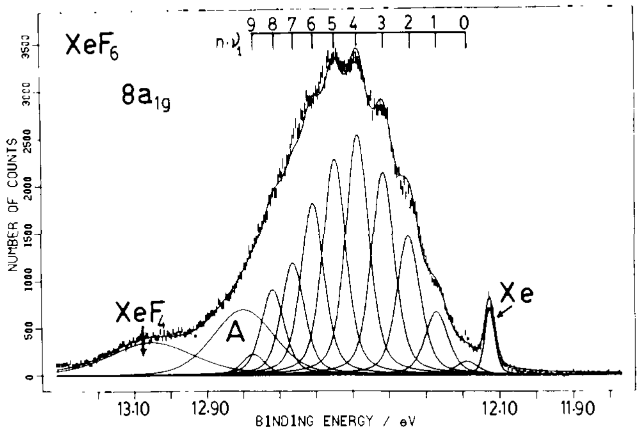

Figure 3. He I photoelectron spectrum of the $8a_{1g}$ orbital of XeF_6.

In order to test this hypothesis, we undertook an Xα-SW calculation (Tables I and II) on XeF_6 in the C_{3v} symmetry group (see below). We found that even for a relatively large distortion of 5° from octahedral the splitting between the two types of fluorines was only ~0.2 eV. This is certainly insufficient to account for the large line width (Figure 1) unless both peaks have half-widths considerably larger than 2.0 eV.

In an additional attempt to resolve the question concerning inequivalent fluorines we obtained the He I spectrum of the HOMO ($8a_{1g}$) in XeF_6. The original spectrum of XeF_6[24] exhibited a very broad band for this level that was interpreted as resulting from the antibonding character of the $8a_{1g}$ orbital. We felt that if we could resolve and analyze a splitting in this level we could obtain useful structural information. It should be noted that the a_{1g} terminology assumes octahedral symmetry. The He I spectrum is presented in Figure 3. The peak at the high binding energy end is due to XeF_4 ($10a_{1g}$) and the small peak at the low binding

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Table II. Xα-SW Ground-State Energies and Charge Distribution in XeF_6

		Xe, %				F, %					
orbital	ground-state energy, eV	s	p	d	f	s	p	d	f	outer, %	inter, %
$8a_{1g}$	9.66	16.58				1.91	73.49			3.03 (s)	4.20
$1t_{1g}$	13.27						89.26			0.98	9.55
$1t_{2u}$	13.77						85.75			0.86	12.54
$7t_{2u}$	13.89	0.11					84.48			1.09 (p)	12.72
$5e_g$	14.24			5.92			86.23			2.59 (d)	5.00
$3t_{2g}$	14.53			1.45			79.96			1.19 (d)	17.37
$6t_{1u}$	17.92		28.76		0.28	3.21	54.08			1.37 (p)	12.31
$7a_{1g}$	24.90	50.82				22.38	17.23			0.95	8.63
$4e_g$	32.31			1.44		92.67				0.66	5.12
$5t_{1u}$	32.84		3.43		0.47	89.01	0.32			0.53	6.19
$6a_{1g}$	34.42	18.24				70.61	1.88			0.37	8.69

energy end is due to Xe $5p_{3/2}$. No evidence for XeF_2 was found in the spectrum. A broad peak (A) has been fit at the high binding energy end of the $8a_{1g}$ progression as the vibrational levels are too close together to resolve.

The $8a_{1g}$ level itself shows an obvious vibrational progression that we have fit reasonably well with a series of peaks. The average spacing between the peaks is $\sim$530 cm^{-1}. Since calculations indicate that the $8a_{1g}$ orbital is strongly antibonding,[24] removal of an electron should excite higher energy vibrations than observed in the neutral molecule. The fact that the orbital is totally symmetric makes the only possible excited vibrational mode the a_{1g} (ν_1) type. The matrix isolation IR spectrum of XeF_6[18] shows four bands in the stretching region at 630, 624, 557, and 506 cm^{-1}. The gas-phase results are shifted to slightly higher energy (10 cm^{-1}). However, the width of the bands make accurate energy determinations very difficult. Pitzer and Bernstein[20] have interpreted these numbers based on C_{3v} geometry for XeF_6. They assign the 630- and 624-cm^{-1} frequencies to the A_1-type T_{1u} and A_{1g} stretches and the 557- and 506-cm^{-1} peaks to the E-type T_{1u} and E_g stretches, respectively. We observe an ion-state vibrational separation of $\sim$530 cm^{-1}, which is considerably lower in energy than the ground-state frequency (624 cm^{-1}). This result tends to contradict the original assignment[24] and implies that the $8a_{1g}$ orbital is actually bonding rather than antibonding. Also, the fact that a large number (>10) of vibrational levels are excited is not consistent with an antibonding orbital where, generally, relatively few vibrational levels are accessible in the slowly sloping attractive region of the ionic potential.[25] It should be pointed out, however, that caution must be exercised when assigning orbital character on the basis of vibrational structure alone. For instance, the $3a_1$ orbital of ammonia, which is nonbonding, exhibits substantial vibrational structure.[26] This is due to the fact that while the $3a_1$ orbital is nonbonding and therefore should not excite vibrations, it is structure determining and removal of an electron produces considerable bending.

It is interesting at this point to consider the hole-state structure of XeF_6. Most of the models developed to explain the ground-state XeF_6 structure involve a lone pair of electrons (presumably Xe $5s^2$) to account for the distortion. In order to determine the composition of the XeF_6 valence orbitals we performed an Xα calculation on the molecule assuming O_h symmetry. The parameters used in the calculation are listed in Table I, and the percent orbital character and ground-state energies are summarized in Table II. These energies are in good agreement with a previous Xα-SW calculation;[27] however, the percent orbital character was not included in the original work. The majority of the Xe 5s character (50.82%, Table II) is located in the $7a_{1g}$ orbital with the remainder being shared between the $6a_{1g}$ (18.24%) and $8a_{1g}$ (16.58%) orbitals. If in fact the distortion is due to a relatively mobile lone pair of electrons, it would seem reasonable that the responsible orbital is the $8a_{1g}$ rather than the much deeper lying $7a_{1g}$ and $6a_{1g}$ orbitals. The crystal-field approach to the problem of Wang and Lohr[28] utilizes the energy gap between the 5s and 5p orbitals (E_{5s-5p}) in Xe^{6+} as one of the parameters used to determine the variation in energy with the amount of distortion from O_h symmetry. They find that a value of 3.5 eV for E_{5s-5p} best describes the molecule. In a subsequent paper Wang and Lohr[29] point out that this energy is very close to the calculated[27] separation (3.42 eV) between the $8a_{1g}$ orbital and the lowest unoccupied orbital ($8t_{1u}$*). Thus, their analysis infers that the distortion is actually due to the $8a_{1g}$ electrons rather than the predominantly Xe 5s orbital ($7a_{1g}$). The same conclusion is reached by Bartell and Gavin,[17] who state that if the $8a_{1g}$ electrons are removed, the molecule is isoelectronic with the known octahedral TeF_6. In that instance the low-lying $8t_{1u} \leftarrow 8a_{1g}$ transition would no longer exist and the pseudo-Jahn–Teller situation would vanish. On the basis of these results, we must conclude that removal of one of the $8a_{1g}$ electrons decreases the distortion from O_h symmetry relative to ground-state XeF_6. Therefore, the vibrational structure associated with the $8a_{1g}$ orbital probably corresponds to an essentially octahedral structure, in which the fluorines are very nearly equivalent.

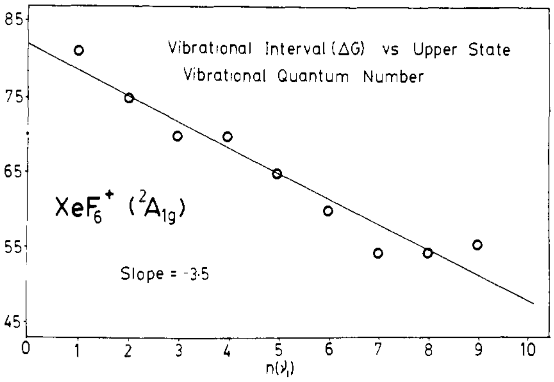

Figure 4. Vibrational interval in the $8a_{1g}$ XeF_6 orbital vs. the upper-state vibrational quantum number.

We also noted a distinct trend in the spacing between adjacent vibrational levels and have plotted the results in Figure 4. The negative slope observed is indicative of positive anharmonicity.[30] Basically this means that the upper state levels are converging as they approach the dissociation limit. Negative anharmonicities are usually associated with bending vibrations where because of steric interactions the restoring force does not become weaker as the amplitude increases.[30]

Neither the Xα results nor the $8a_{1g}$ valence structure on XeF_6 provides evidence indicating a chemical environment that might give rise to significantly inequivalent fluorines. In light of this, a more comprehensive approach was attempted to explain the

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Table III. Parameters Used in the Calculation of $-D(\mathrm{XNe})^+$ [h]

compd	E_B[F(1s)], eV	fwhm, eV	ΔH_f(XF), eV	ΔH_f(X$^+$), eV	$-D(\mathrm{XNe})^+$, eV
HF	694.0[a]	1.48[a]	−2.81[d]	15.9[g]	−2.1
KrF$_2$	688.9[a]	1.41[a]	0.67[e]	13.3[e]	−1.1
F$_2$	696.7[b]	1.2[b]	0.0[d]	18.3[g]	1.1
CH$_3$F	692.4[a]	1.45[a] (1.36)[b]	−2.43[d]	11.3[g]	1.4
XeF$_2$	691.2[a]	1.50[a]	−1.22[f]	10.9[f]	1.8
CF$_4$	695.0[a]	1.85[a] (1.83)[b]	−9.59[d]	5.65[g]	2.3
SF$_4$	695.3 (eq)[c] 692.9 (ax)[c]	1.87 (eq)[c] 2.15 (ax)[c]	−8.09[d]	4.94[g]	(eq) see text 2.4 (ax)
XeF$_4$	692.1[a]	1.80[a]	−2.50[f]	9.81[f]	2.4
ClF$_3$	694.8 (eq)[c] 692.2 (ax)[c]	1.74 (eq)[c] 2.00 (ax)[c]	−10.3[d]	1.65[g]	(eq) see text 2.9 (ax)
SF$_6$	695.0[c]	2.01[c]	−12.7[d]	1.95[g]	3.0
CF$_3$H	694.1[a]	1.95[a]	−7.16[d]	6.20[g]	3.3
XeF$_6$	693.3[a]	2.63[a]	−3.90[f]	7.85[f]	4.2

[a] This work. [b] References 8-10. [c] Reference 14. [d] Reference 37. [e] Reference 38. [f] Reference 39. [g] Reference 34. [h] $-D(\mathrm{XNe})^+$ is, of course, the dissociation energy to the ground-state fragments; as one of the referees pointed out, the dissociation *may not* always go to ground-state fragments.

anomalously broad F 1s half-width in XeF$_6$ and the variation in F 1s peaks for the other compounds.

Equivalent Cores Treatment of the F 1s Line Widths. Because of the difficulty, time, and cost involved in the detailed hole-state potential analysis of Goscinski et al.,[5] we have developed a relatively simple method based on the equivalent cores formalism[31] to correlate the F 1s broadening effects. F 1s binding energies and half-widths for 12 compounds are presented in Table III.

In the equivalent cores procedure,[10,31] the removal of a core electron is taken as being approximately equal to the addition of a proton to the nucleus. Thus, a core hole species is replaced by the equivalent core of the next element in the periodic table (e.g., $C^{*+} \equiv N^+$, $N^{*+} \equiv O^+$, etc., where * denotes a 1s core hole). While in fact this core-exchange energy has been found to be sizeable (6.0 eV for $C^*H_4^+ \rightarrow NH_4^+$),[32] it is essentially the same for a series of compounds. The problem is to derive a parameter that will be proportional to the slope of the core ionized state. The photoionization reaction for a typical fluoride (XF) is

$$\mathrm{XF} \xrightarrow{h\nu} \mathrm{XF}^{*+} + e^- \qquad (4)$$

The slope of the upper state is then $\partial E_{\mathrm{XF}^{*+}}/\partial R$, which could be plugged into eq 3 to obtain the fwhm. It would seem reasonable to assume that the magnitude of the slope will be related to the dissociation energy for the reaction

$$\mathrm{XF}^{*+} \rightarrow \mathrm{X}^+ + \mathrm{F}^* \qquad (5)$$

(In this reaction we have transferred a valence X electron to F* during dissociation because of the high electronegativity of core ionized fluorine.) It is not possible of course to directly calculate the energy of eq 5 because of the lack of thermochemical data on core-ionized species such as XF^{*+}. In order to circumvent this problem the equivalent cores method is employed as follows:

$$\mathrm{XF} \xrightarrow{h\nu} \mathrm{XF}^{*+} + e^- \qquad E_B[\mathrm{F(1s)}] \qquad (6)$$

$$\mathrm{XF}^{*+} + \mathrm{Ne} \rightarrow \mathrm{XNe}^+ + \mathrm{F}^* \qquad E_{\mathrm{CE}} \text{ (core exchange energy)} \qquad (7)$$

$$\mathrm{X}^+ + \mathrm{F}^* + e^- \rightarrow \mathrm{XF} \qquad \Delta H_f(\mathrm{XF}) - \Delta H_f(\mathrm{X}^+) - \Delta H_f(\mathrm{F}^*) - \Delta H_f(e^-) \qquad (8)$$

Summing eq 6, 7, and 8 yields

$$\mathrm{Ne} + \mathrm{X}^+ \rightarrow \mathrm{XNe}^+ \qquad -D(\mathrm{XNe})^+ \qquad (9)$$

$$-D(\mathrm{XNe})^+ = E_B + \Delta H_f(\mathrm{XF}) - \Delta H_f(\mathrm{X}^+) + E_{\mathrm{CE}} - \Delta H_f(\mathrm{F}^*) - \Delta H_f(e^-) \qquad (10)$$

The quantity of interest is $-D(\mathrm{XNe})^+$, which is related to the various energies involved in eq 10. The last three terms are constant for all fluorides but for the reasons already given cannot be directly determined. It is possible to calculate the value of the constant through the use of the HF cycle:

$$\mathrm{HF} \xrightarrow{h\nu} \mathrm{HF}^{*+} + e^- \qquad E_B[\mathrm{F(1s)}] \qquad (11)$$

$$\mathrm{HF}^{*+} + \mathrm{Ne} \rightarrow \mathrm{HNe}^+ + \mathrm{F}^* \qquad E_{\mathrm{CE}} \qquad (12)$$

$$\mathrm{H}^+ + \mathrm{F}^* + e^- \rightarrow \mathrm{HF} \qquad \Delta H_f(\mathrm{HF}) - \Delta H_f(\mathrm{H}^+) - \Delta H_f(\mathrm{F}^*) - \Delta H_f(e^-) \qquad (13)$$

Summing eq 11, 12, and 13 yields[10]

$$\mathrm{Ne} + \mathrm{H}^+ \rightarrow \mathrm{HNe}^+ \qquad -D(\mathrm{HNe})^+ = -2.085 \text{ eV} \qquad (14)$$

$$E_{\mathrm{CE}} - \Delta H_f(\mathrm{F}^*) - \Delta H_f(e^-) = -D(\mathrm{XNe})^+ - E_B - \Delta H_f(\mathrm{XF}) + \Delta H_f(\mathrm{X}^+) = -677.3 \text{ eV} \qquad (15)$$

where the quantities used in the calculation are listed in Table III.

Since the energy of reaction 14 is simply the proton affinity of neon and the other terms on the right hand side of eq 15 are easily obtained, the value of the constant term is calculated to be −677.3 eV.

Using this constant, we have calculated $-D(\mathrm{XNe})^+$ for a number of fluorides and summarized the results in Table III. Both HF and KrF$_2$ possess negative values for $-D(\mathrm{XNe})^+$ while all of the remaining compounds are positive. Within the equivalent cores framework, a negative value represents a bound state for XNe$^+$ while a positive value represents an unbound or dissociative XNe$^+$ system. Pictorially, the transitions to the two types of final states are shown in Figure 5. The important thing to note is that in both cases the observed fwhm will be a function of the slope of the upper state and the corresponding vibrational band envelope. As shown by Goscinski et al.,[5] for CF$_4$ and CH$_3$F, probably just the symmetrical a$_1$ modes will be important in determining the line broadening. Assuming, then, that the magnitude of $-D(\mathrm{XNe})^+$ is proportional to the slope of the upper state, we have plotted these values vs. the F 1s fwhm values in Figure 6. On the right hand side of the figure [$-D(\mathrm{XNe})^+$ = positive], a rather good correlation is evident ($r^2 = 0.87$) considering the assumptions and the large possible errors in the ΔH values. The linear least-squares best fit to the data yields an intercept of 0.85 eV and a slope of 0.41. At the intercept, $-D(\mathrm{XNe})^+ = 0$, there will be little or no interaction between Ne and X$^+$. The upper state, then, will exhibit close to zero slope and there will be little or no vibrational contribution to the observed line width. In this instance, then, the fwhm should primarily consist of contributions from the X-ray source, the analyzer, and the inherent F 1s lifetime width. The Al K$\alpha_{1,2}$ width is 0.85 eV,[1] and we have found that for our analyzer the resolution is best described by the relation $E_{\mathrm{KE}}/\Delta E_{\mathrm{fwhm}} = 5000$. Using this equation and the fact that the kinetic energy is ~793 eV, we calculate an analyzer contribution of 0.16 eV. The lifetime width of the F 1s level is ~0.2 eV,[33] which when

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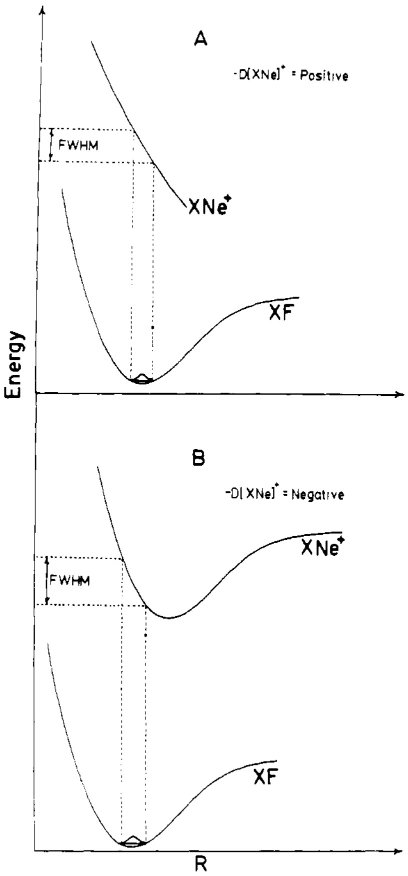


Figure 5. Pictorial representation of transitions to (a) unbound states, (b) bound states.

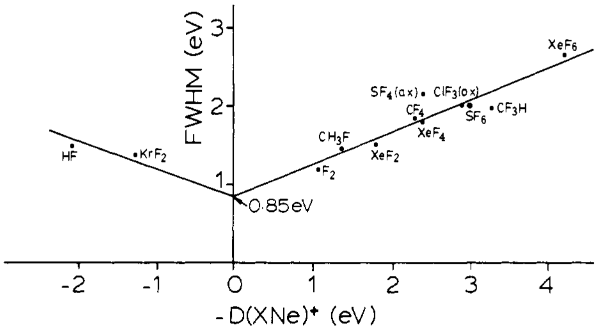


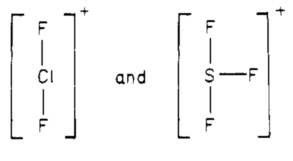
Figure 6. F 1s full width at half-maximum (fwhm) vs. the dissociation energy $-D[\mathrm{XNe}]^+$. The intercept, slope, and r^2 value for the right hand side of the diagram are 0.85 eV, 0.41, and 0.87, respectively.

combined with the other two contributions allows us to calculate the predicted fwhm in lieu of vibrational broadening:

$$\begin{aligned}\mathrm{fwhm} &= (0.85^2 + 0.16^2 + 0.2^2)^{1/2}\\ &= 0.89\ \mathrm{eV}\end{aligned}$$

The fact that this value is quite close to that obtained from the correlation (0.85 eV) supports the analysis presented here. We have assumed for the best fit line with negative values of $-D(\mathrm{XNe})^+$ (Figure 6) that the intercept on the fwhm axis (0.85 eV) is common to both halves of the figure.

Another interesting facet of this correlation concerns compounds with inequivalent fluorines such as $\mathrm{ClF_3}$ and $\mathrm{SF_4}$. In Figure 6, we have only included the *axial* fluorines because the heats of formation for the $\mathrm{X^+}$ ions [$\Delta H_f(\mathrm{ClF_2}^+) = 1.65$ eV; $\Delta H_f(\mathrm{SF_3}^+) = 4.94$ eV] have been determined[34] for the ground-state configuration of these ions, which in both cases involves the loss of an *equatorial* fluorine, i.e.



ΔH_f values are not known, and thus $-D(\mathrm{XNe})^+$ cannot be determined from eq 15 to obtain ΔH_f for the above cations. Using the fwhm for the equatorial F in Table III, we obtain $-D(\mathrm{XNe})^+$ values from the linear relationship fwhm = 0.85 – 0.41 $D(\mathrm{XNe})^+$ derived above. We obtain 2.2 eV for $-D(\mathrm{ClF_2Ne_{eq}})^+$ and 2.5 eV for $-D(\mathrm{SF_3Ne_{eq}})^+$. From eq 15, the heats of formation for the $\mathrm{ClF_2}^+$ and $\mathrm{SF_3}^+$ ions drawn above are 5.0 and 7.4 eV, respectively. These are more positive by 3.4 and 2.5 eV, respectively, than the ΔH_f values for the ground states (Table III). It is interesting to note that the above values are similar to those calculated previously by Shaw et al.[14] from binding energies and the equivalent cores treatment.

An additional piece of interesting information that can be extracted from this correlation concerns relative oxidation strengths. Both $-D(\mathrm{XNe})^+$ and consequently the fwhm are a measure of the Lewis acidity of $\mathrm{X^+}$ toward neon, e.g., $\mathrm{F^+ > XeF^+ > XeF_3^+ > XeF_5^+}$. Studies carried out on adduct formation with the fluorides of xenon indicate that the relative stabilities of the XeF_n molecules toward the loss of fluoride ion is $\mathrm{XeF_4 \gg XeF_2 > XeF_6}$.[37] Our equivalent cores analysis utilizing the $-D(\mathrm{XNe})^+$ values actually calculates the relative stabilities of the $\mathrm{XeF}_{n-1}\mathrm{Ne}^+$ compounds toward the loss of neon, $\mathrm{XeFN^+ > XeF_3Ne^+ > XeF_5Ne^+}$. This ordering, while differing from that found for adduct formation, is identical with the ordering found in photoionization mass spectroscopic work on the relative stabilities of the $\mathrm{XeF}_n{}^+$ ions toward the loss of a fluorine atom, $\mathrm{XeF_2^+ > XeF_4^+ > XeF_6^+}$.[38,39] It is not immediately obvious why the relative stabilities of the neutral molecules toward the loss of fluoride ion should be different from that observed for charged species toward the loss of neon or fluorine atoms. However it could be related to solid-state effects experienced during adduct formation.

Conclusion

Our equivalent cores treatment of the F 1s line widths strongly suggests that vibrational broadening is the dominant line-broadening mechanism in these compounds. This treatment should be useful for quantifying line widths for other core levels such as S 2p, N 1s, and O 1s and obtaining heats of formation of unusual cations and relative Lewis acidities for compounds of these elements.

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Registry No. $\mathrm{KrF_2}$, 13773-81-4; $\mathrm{XeF_2}$, 13709-36-9; $\mathrm{XeF_4}$, 13709-61-0; $\mathrm{XeF_6}$, 13693-09-9; $\mathrm{CH_3F}$, 593-53-3; $\mathrm{CF_3H}$, 75-46-7; $\mathrm{CF_4}$, 75-73-0; HF, 7664-39-3.

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