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Fluorine 1s Correlation States in the Photoionization of  
Hydrogen Fluoride: Experiment and Theory\*

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ABSTRACT -- The x-ray photoemission spectrum of the F 1s region of gaseous HF was measured using  $AlK\alpha_{1,2}$  radiation. Several satellite ("shake-up") peaks were observed at  $\sim 25$ - $35$ eV higher binding energy than the main F 1s peak. The spectrum was interpreted in terms of a many-electron theory that includes configuration interaction (CI) in both the hole state and the ground state. A CI calculation yielded eleven physically meaningful excited states based on the  $HF^+$  (F 1s hole) state. Six were predicted to have intensities over 0.1% that of the main peak. The four most intense of these were clearly present by visual inspection of the spectrum. Six were readily fitted by the addition of constraints. Derived intensities were in nearly perfect agreement with theory if ground-state CI was included. The four most intense peaks can be crudely interpreted as arising from  $3\sigma$  to  $4\sigma$ ,  $1\pi$  to  $2\pi$ , and  $1\pi$  to  $3\pi$  excitations, but careful inspection of the orbitals shows that these designations are oversimplified.

## I. INTRODUCTION

Photoemission spectra of atomic core levels in atoms and molecules yield for each core level  $j$  a main peak at an electron kinetic energy

$$K = \hbar\omega - E_B^{(0)}. \quad (1)$$

Here  $\hbar\omega$  is the photon energy and  $E_B^{(0)}$  is the binding energy of core level  $j$ . This main peak corresponds to a special atomic or molecular ion final state. In a single-determinant description, this state would be formed from the ground state by removing an electron from orbital  $j$  and allowing the wave functions of the passive electrons to relax adiabatically (i.e., without changing their quantum numbers).

If  $h\nu$  is substantially larger than  $E_B^{(0)}$ , additional weak satellite peaks may also be observed at higher binding energies  $E_B^{n'}$ . Qualitatively, one usually describes these states as arising from at least a two-electron excitation from the ground state (ionization accompanied by "shakeup"). A quantitative theoretical treatment of the transition cross section to such states, however, shows that one-electron descriptions may be misleading. The cross section for such a transition owes much of its strength to many-body effects. In particular, configuration interaction (CI) in both the initial and final state is required; hence the latter are more accurately described as "correlation states", and the satellite peaks as "correlation peaks".

The theoretical formalism for calculating correlation-state spectra was described in the preceding paper<sup>1</sup> (hereafter called I). We report in the present paper a complete study of the fluorine 1s correlation-state spectra in gaseous HF. To our knowledge this is the first case in which

several of the theoretical nuances developed in I have been applied. It is also the first case showing quantitative agreement between experiment and theory.

Experimental procedures and results are given in Sec. II. Section III describes both the means of obtaining the necessary wavefunctions and the method used to compute intensities. Conclusions are drawn in Sec. IV.

## II. EXPERIMENTAL

The gaseous sample was obtained by evaporation of 99.9% + pure liquid HF, purchased from Matheson Gas Products, Inc. At 26°C the association constants of HF are:<sup>2</sup>



with pressures expressed in torr. Thus oligomerization is unimportant at the pressures of < 1 torr used in this work.

The photoelectron spectra were obtained using Al  $K\alpha_{1,2}$  x-rays (1486.6 eV) on the 50 cm radius Berkeley iron-free magnetic spectrometer.<sup>3</sup> Spectral data points were taken at 0.4 eV energy increments, at pressures of 0.50 and 0.350 microns (Fig. 1). The analyzer chamber was maintained at a pressure of approximately  $10^{-5}$  torr. The high pressure spectrum was used to determine which of the satellites of the F 1s main line were caused by inelastic electron collisions since the intensities of these peaks should increase with pressure. If the low pressure spectrum (Fig. 1b) is subtracted from the high pressure spectrum (Fig. 1a), with appropriate weighting to equalize the main F 1s peaks, the result is an inelastic electron loss spectrum.

The low pressure spectrum was fitted (Fig. 2) using a non-linear

least squares program which automatically took into account the (weak) Al  $K\alpha_3$  and  $K\alpha_4$  components as well as the slight change of the energy window caused by the magnetic spectrometer (which produces spectra linear in momentum). The main peak, corresponding to the F 1s hole state, was fitted best by a sum of three Lorentzian functions and these were used as the fundamental form for the "correlation" peaks.

No attempt was made to locate satellites with intensity 0.1% or less of the main peak. It was necessary to fix the area ratios and separations of states 7 and 10 relative to their large neighbors (5 and 9 respectively). Theoretical area ratios and separations, described below, were used for these two cases.

Because of the large number of unknowns, the energy positions and full widths at half-maximum (FWHM) of a few peaks were initially fixed, and the fitting program was constrained to vary only the parameters for those remaining. These newly found optimum parameters were then frozen and the rest of the set (those originally fixed) varied. This successive approximation technique was continued until a self-consistent set of parameters was found. The quality of the fit was judged from the statistical  $\chi^2$  and visual examination of the plot (Fig. 2).

The results in Table I indicate that the theoretical intensities are in excellent agreement with experiment. Theoretical energies, relative to the main line, are 2.1 to 3.5 eV higher than experiment.<sup>4</sup> The width of the satellites increases with greater separation from the main peak, as the double ionization ("shake-off") limit is approached.

### III. THEORETICAL

The correlation-peak spectrum was calculated using the theoretical

formalism described in I.<sup>5</sup> Two major levels of sophistication were used for the wavefunctions necessary in this work. First, configuration interaction among the ionic final states was considered, with the ground state represented by a single Slater determinant. In the next step, CI in the ground state was also included. For each of these cases the relative intensities of the correlation peaks were computed in the overlap approximation.

It was shown in I that, except for terms to be discussed in Appendix I (which are small for core-level satellites), the dipole and the N-electron sudden approximations give identical results in the overlap approximation. Results are displayed in Table I for final state CI (Method A) and for initial state CI (Method B). In addition an estimate of the variation in the energy-dependent term was obtained assuming the photoelectron continuum function to be represented by a plane wave. This causes the relative intensities calculated from the dipole and N-electron sudden approximation to be very slightly different. The variation in the energy-dependent factor,  $Q(E)$ , is shown in Table II. The product of this factor and the overlap term gives the final set of relative intensities shown in Table II.

The means of calculating the various wavefunctions are discussed in IIIA followed by a description of the one-electron basis set in IIIB. Section IIIC deals with the overlap and energy-dependent portions of the cross section.

#### A. The Wavefunctions

A set of SCF orbitals was found for the ground state occupancy

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 ({}^1\Sigma^+),$$



by using an iterative natural orbital "annihilation of singles" technique.<sup>6,7</sup> The energy obtained with this technique is identical to that which would follow from a standard Hartree-Fock-Roothaan calculation. The orbitals, however, are natural orbitals instead of the standard canonical set which diagonalize the Fock matrix. They were transformed into the canonical set by the appropriate unitary transformation.

Using the canonical orbitals found in this way as trial vectors, a further "annihilation of singles" calculation was carried out on the ion  $\text{HF}^+$  at the internuclear separation of the neutral molecule. This yielded a wavefunction for the single configuration  $1\sigma^1 2\sigma^2 3\sigma^2 1\pi^4 ({}^2\Sigma^+)$ , which will be termed the "reference state." It corresponds to the F 1s hole state, and represents the wavefunction which would be found by applying the Hartree-Fock-Roothaan equations to this open shell single determinant.

To obtain appropriate wavefunctions for the excited states in the vicinity of the reference state, a configuration expansion was employed. All single excitations with respect to the reference state which possessed  ${}^2\Sigma^+$  symmetry were included. For our basis set of 14 $\sigma$  and 6 $\pi$  molecular orbitals, this results in 66 configurations. These can be represented

$$\begin{array}{ll} 2\sigma^2 3\sigma^2 m\sigma 1\pi^4 & (1\sigma \rightarrow m\sigma) \\ 1\sigma^1 2\sigma 3\sigma^2 m\sigma 1\pi^4 & (2\sigma \rightarrow m\sigma) \\ 1\sigma^1 2\sigma^2 3\sigma m\sigma 1\pi^4 & (3\sigma \rightarrow m\sigma) \\ 1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 n\pi & (1\pi \rightarrow n\pi). \end{array}$$

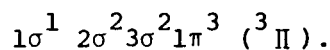
For the last three types there are three electrons outside closed shells; thus two  ${}^2\Sigma^+$  configurations exist for each single excitation. Both of these configurations were included in the expansion.<sup>8</sup>

With the one-electron basis set defined by the orbitals for the F 1s

reference state, the Hamiltonian matrix within this configuration space was formed and diagonalized. We assume that the resulting roots and eigenvectors are reasonably good approximations to those excited  $2\Sigma^+$  states of  $\text{HF}^+$  that lie in the energy region near the reference state.<sup>9</sup>

Initially we hoped that by limiting the expansion to single excitations, each excited state could be rather straightforwardly interpreted in terms of a one-electron transition from the reference state. We found, however, that when the virtual canonical orbitals of the reference state were used in the one-electron basis, several excitations mixed strongly in the eigenvectors of interest. In other words, the unoccupied eigenvectors from the hole-state calculation are not very good approximations to the excited-state orbitals. For this reason, the virtual canonical orbitals were transformed into a set appropriate for describing the motion of an electron in the field of an N-2 electron core. The orbitals found in this way reflect more closely the potential experienced by the "excited" electron. This transformation has been used in similar problems previously,<sup>10</sup> and we will not discuss it here. This new starting set gave, in most cases, excited states which could be well described in terms of one-electron excitations from the reference state determinant.

The description of the ionic states was concluded by performing a final SCF calculation on the ion  $\text{HF}^{2+}$  in the configuration



The energy of this state relative to the reference state is interpreted as the threshold of "shake-off" phenomena.

A brief discussion of the rationale involved in the computation of the initial state CI wavefunction seems in order. After the work on ionic HF,

we knew the general nature of the correlation states which could be described by our basis set. This dictated the choice of the configuration expansion for the ground state. Our approach was to reduce the ground state virtual space to those orbitals that most closely resembled the orbitals which were important in describing the correlation states. This reduction was, of course, inherently subjective, but necessary due to the size limitations of our computer program. All single and double excitations from the valence orbitals ( $3\sigma$ ,  $1\pi$ ) into this reduced virtual space (generating a total of 105 configurations) were included.<sup>11</sup>

#### B. The Basis Set for Hydrogen Fluoride

The basis set finally chosen consisted of normalized Slater-type orbitals (STO's). It is set out in Table III. The requirements that the basis set must satisfy are twofold. First, it was found that a double-zeta description of the valence orbitals is necessary to account correctly for the effects of electronic relaxation in the F  $1s$  hole state. Furthermore, the proper Rydberg-type orbitals must be included in the basis set in order to obtain a reliable description of the excited states. We approached this problem by augmenting the double zeta basis set of Huzinaga and Arnau<sup>12</sup> for the fluorine atom with a 3d polarization function ( $\xi = 2.500$ ) and two H  $1s$  functions (exponents 1.000 and 1.500). To this set we systematically added Rydberg-type orbitals on the fluorine atom. A total of eight calculations were performed in this way. The final set consisted of fourteen sigma- and six pi-type functions.

In the first few calculations, Rydberg orbitals on fluorine were chosen on the basis of Slater's rules. One might expect, in the united-atom limit, that the orbitals of the  $\text{He}^+$  ion ( $n \geq 3$ ) would be appropriate

for the Rydberg states of the F 1s hole state. We found, however, that the exponents estimated in this way were too diffuse.<sup>13</sup> The final set contains orbitals with exponents slightly larger than those suggested by Slater's rules.

Not all of the excited states that can be calculated for a given basis set will have physical significance. Our final basis gave stable energies and transition moments, with respect to addition of further orbitals and slight modifications of the exponents of existing orbitals, for those excited states which we felt were physically reasonable. It does not represent an optimized set of orbitals; rather it is one which is sufficiently flexible to meet our particular needs. The philosophy of our approach was to employ a large enough basis set in the HF<sup>+</sup>/CI calculation to reproduce the lowest 10 "shake-up" states reliably both in energy and in orbital composition (hence in peak intensity). These are the states that appear clearly in the experimental spectrum before the "shake-off" ionization limit.

An indication of the completeness of the basis set for at least two of the states of interest here is afforded by comparison with previous work. The final set chosen gives an SCF energy of -100.0553 a.u.<sup>14</sup> for the  $1\Sigma^+$  ground state of HF. The near Hartree-Fock result of Cade and Huo<sup>15</sup> is -100.0703 a.u. The same basis yields an energy of -74.5670 a.u. for the F 1s hole state, to be compared with Schwartz's result of -74.5365 a.u.<sup>16</sup>. The calculated F 1s binding energy is 693.5 eV, which is slightly higher than the value of 693.3 eV reported by Schwartz. Our<sup>3</sup> shakeoff limit falls at -73.2872 a.u., or 34.8 eV above the primary hole state.

The compositions of the molecular orbitals which are most important for describing "shakeup" phenomena in HF are given for the ground state and the ionic states in Table IIIA and Table IIIB respectively.

### C. Intensity Calculations

The intensity of each final-state peak relative to that of the main peak was first calculated in the overlap approximation (Eq. 24c or Eq. 27c from I.) If only final-state CI was considered (Method A), the relation

$$\frac{I(n')}{I(0)} = \frac{\left| \sum_n C_{n'n} S_n^{11} \right|^2}{\left| \sum_n C_{0n} S_n^{11} \right|^2} \quad (2)$$

is appropriate. The extension of the theory to include configuration interaction in the initial-state (Method B) leads to

$$\frac{I(n')}{I(0)} = \frac{\left| \sum_{n,m} C_{n'n}^* D_{0m} S_{nm}^{11} \right|^2}{\left| \sum_{n,m} C_{0n}^* D_{0m} S_{nm}^{11} \right|^2} \quad (3)$$

Here  $C_{n'n}$  and  $D_{0m}$  are the coefficients of the configurations (n and m) in the eigenvectors of the final and initial states, respectively. For HF these would have the form

$$\begin{aligned} |\psi_f^{(n')}\rangle &= C_{n'0} | 1\sigma 2\sigma^2 3\sigma^2 1\pi^4 ({}^2\Sigma^+) \rangle \\ &+ C_{n'1} | 1\sigma 2\sigma^2 3\sigma 4\sigma 1\pi^4 (A {}^2\Sigma^+) \rangle \\ &+ C_{n'2} | 1\sigma 2\sigma^2 3\sigma 4\sigma 1\pi^4 (B {}^2\Sigma^+) \rangle \\ &+ \dots \end{aligned}$$

$$\begin{aligned}
 |\psi_i^{(0)}\rangle &= D_{00} |1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 ({}^1\Sigma^+)\rangle \\
 &+ D_{01} |1\sigma^2 2\sigma^2 3\sigma 4\sigma 1\pi^4 ({}^1\Sigma^+)\rangle \\
 &+ \dots
 \end{aligned}$$

where, for the final state  $|\psi_f^{(n')}\rangle$ , the two linearly independent double spin functions which can be constructed from the orbital occupancy are denoted by A and B.

The overlap functions  $S_{nm}^{11}$  were discussed in I. Here they actually refer to a sum of determinantal overlap integrals, the nature of the sum being determined by the expansion coefficients of the Slater determinants in the configuration. For HF the superscripts "11" refer to the deletion of the row containing electron 1 and the column containing the basis function  $1\sigma$  from the ground state determinant(s).

Analysis of the energy dependent factor in the cross section,  $Q(E)$ , requires specification of the photoelectron continuum function  $|\chi\rangle$ . For the purposes of estimation, we chose the plane wave approximation

$$\chi = (2\pi)^{-3/2} e^{ik \cdot r}$$

For a given photon energy, this term in the dipole cross section is

$$\begin{aligned}
 Q(E)_{\text{DIPOLE}} &= \rho(E) \left| \langle \phi_{1\sigma} | \nabla | \chi \rangle \right|^2 \\
 &\propto k^2 \rho(E) \left| \langle \phi_{1\sigma} | \chi \rangle \right|^2
 \end{aligned} \tag{4}$$

where  $k$  is the wavevector of the photoelectron,  $\rho(E)$  is the density of final continuum states (proportional to  $k$ ), and  $\langle \phi_{1\sigma} | \chi \rangle$  is the overlap of the  $1\sigma$  orbital (a linear combination of STO's) with the plane wave  $|\chi\rangle$ .

The N-electron sudden approximation gives

$$Q(E)_{\text{SUDDEN}} = \rho(E) \left| \langle \phi_{1\sigma} | \chi \rangle \right|^2 . \quad (5)$$

Both of these expressions are slowly varying for the slight changes in  $k$  across the manifold of the HF correlation states. They are displayed in Table II.

#### IV. CONCLUSIONS

The conclusions drawn below refer specifically to the F 1s correlation-state peaks in the high-energy XPS spectrum of HF. We believe that most of them are more generally true for comparable spectra, but the exact extent to which they apply can be ascertained better following theoretical analysis of additional cases.

First and perhaps of most importance, the excellent agreement between experiment and Method B (Table I) provides strong evidence that the overlap approximation embodied in Eq. 3 is adequate to describe such a high-energy core-level correlation-state spectrum. Since Eq. 3 could be derived from Eq. I.14, without reference to the dipole operator itself, this implies that even the sudden approximation (SA) would give an adequate representation of the relative intensities in the experimental spectrum.

The corollary conclusion is that initial-state CI must be included, since Method A (Table I) gives poor intensity predictions. This is entirely expected in view of the discussion in I, but it has not been recognized in previous work on core level satellite spectra. Examination of Table II and, of course, the results of the overlap approximation, imply that the energy-dependent factor in the cross section can safely be neglected at these energies. At lower photon energies, however, these

terms might be expected to become more important. It is difficult to say at what point they would no longer be negligible, and, perhaps more importantly, at what point the plane wave approximation itself becomes poor. Our results, in fact, do not imply that the plane wave approximation is good even at these energies. They simply suggest that the energy dependence -- whatever its form -- is slowly varying. The usefulness of the plane wave approximation is an important question at the present time since several theoretical models for predicting the intensities of molecular orbital photoemission spectra use either it or a closely related type of continuum function. Further work on this point is in progress in our laboratory.

The primary components of the dipole cross section --  $Q(E)$  and the overlap integral  $S_n^{11}$  -- have already been discussed. There are additional terms in the cross section, however, and in Appendix I we report the results of calculations which evaluate the leading corrections for a few of the states of HF studied here. They are all found to be negligible at the photon energies used in our experiment.

It is interesting to interpret the correlation peak intensities in terms of "shake-up" excitation into virtual orbitals. An examination of Table IV shows that the first two correlation states (1 and 2) can be described fairly well as arising from the  $3\sigma \rightarrow 4\sigma$  transition. These two final states are describable as molecular valence states, the remainder of the spectrum corresponding primarily to Rydberg-like states. Only state 2 of this pair is predicted to have an observable intensity, and it is indeed the first state observed in the experimental spectrum. It seems reasonable to assert that the relatively low intensity of this



transition is attributable to the charge transfer nature of the excitation. The  $3\sigma$  orbital is the bonding combination of the F(2p) and H(1s) orbitals and is largely localized on the fluorine atom, while the  $4\sigma$  is the anti-bonding combination and is primarily hydrogen-like. Since the orbitals have their large components in different regions of space, one would expect a small overlap. This interpretation seems plausible, but there are also more subtle effects that contribute substantially to the cross section. These are the small admixture of the  $1\pi \rightarrow 2\pi$  excitation into state 2, the even smaller admixture of the reference state, and the effect of configuration interaction in the initial state. This last point is very important and can be seen quite clearly in Table I. The inclusion of initial state CI (Method B) nearly doubles the predicted intensity of state 2 relative to the primary hole state.

The most intense peak in the spectrum, state 5, corresponds to the  $1\pi \rightarrow 2\pi$ , or  $F(2p_{\pi}) \rightarrow F(3p_{\pi})$  excitation. Its counterpart, state 3, is also relatively intense. The next most intense peak in the spectrum is state 9, the  $F(2p_{\pi}) \rightarrow F(4p_{\pi})$  excitation. These results, of course, would be expected on the basis of a simple one-electron overlap model.

Satellites with smaller intensities are less predictable. State 7 is primarily attributable to the  $3\sigma \rightarrow 5\sigma$  excitation. It would be tempting to say that since the  $5\sigma$  orbital is F(3s)-like, there should be very little overlap with the  $3\sigma$  orbital in the ground state (which is mainly  $F(2p_{\sigma})$ -like), and this causes the small intensity of state 7. These arguments, however, are probably oversimplified since there is a fairly large component of  $3\sigma \rightarrow 6\sigma$  ( $F2p_{\sigma} \rightarrow F3p_{\sigma}$ ) in the wavefunction. Configuration mixing makes it nearly impossible to give rough *a priori* estimates of intensities. For example, the  $3\sigma \rightarrow 6\sigma$  excitation is important in state 8, and it might therefore be expected to be rather intense. It is not.

The  $F(2p_{\sigma}) \rightarrow F(4s)$  excitation, state 10, on the other hand, has a much larger intensity. The reasons for these differences in overlap are complex, and are tied into the specific nature of configuration mixing in these excited states. Since the configurations enter into the wavefunction with a phase, they can either add intensity to the predominant configuration, or cancel what intensity the dominant configuration might supply. These problems are expected to be more severe in molecules than atoms since there is generally a much denser excited-state manifold in the molecular species.

Finally, we note that the HF molecule is isoelectronic with the Neon atom. One might therefore expect to see some similarities in their satellite spectra. In Figs. 3a and 3b we have drawn a bar spectrum of the most intense satellites in Ne<sup>17</sup> and HF. Above each bar we have assigned an orbital which serves to roughly identify the final state.

The most intense satellites in the Ne 1s spectrum are derived from  $2p \rightarrow np$  excitations. If one imagines the two nuclei in HF being adiabatically compressed into a united atom, the  $3\sigma$  and  $1\pi$  orbitals of the molecule correlate with Ne 2p while  $4\sigma$  and  $2\pi$  correlate with the Neon 3p orbital. Since the major intensity in neon comes from the  $2p \rightarrow 3p$  excitation, it is not surprising that the most intense peaks in HF arise from the  $3\sigma \rightarrow 4\sigma$  and  $1\pi \rightarrow 2\pi$  excitations. The  $(1\pi \rightarrow 4\pi)$  state in HF is also relatively intense and correlates with the  $2p \rightarrow 4p$  excitation in the united atom.

Another qualitatively interesting comparison is to consider the "equivalent cores" analog of the F 1s hole state in HF, i.e. the species  $(NeH)^+$ . The charge distribution in this system is presumably intermediate

in character between the two extremes  $\text{Ne} - \text{H}^+$  and  $\text{Ne}^+ - \text{H}$ , with the latter being the more chemically reasonable. The correlation states of HF should thus be similar to the excited states of  $\text{Ne}^+$ , inasmuch as the hydrogen nucleus is adequately shielded by its electron. The states of  $\text{Ne}^+$  derived from  $2p \rightarrow 3p$  excitations<sup>18</sup> are shown diagrammatically in Fig. 3c. They have been given intensities based on the total degeneracy of each state. This simple picture seems to work quite well, as can be seen by comparing Fig. 3c to Fig. 3b. Although no detailed correlation between specific states can be drawn, this model reproduces the observed shift in HF vs. Ne toward smaller satellite separation from the primary state.

In summary, the correlation-peak spectrum of HF can be calculated quite satisfactorily in the overlap approximation. The intensities of the correlation peaks are very dependent upon the effects of configuration interaction in both the initial and final states. At present, quantitative predictions of such spectra based on simple one-electron models seem doomed to failure. Even qualitative estimates and assignments are very difficult considering the importance of configuration interaction in the final state. The effect of CI in the initial state is to increase the intensities of the shakeup states at the expense of the primary hole state. For HF, the shakeup states are all roughly twice as intense once initial state CI is included.

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Appendix I

In the preceding paper (I), a formalism for the photoemission cross section was presented in which the usual assumption of "frozen orbitals" was not made. This introduced a number of additional terms (Eq. 17) not present in the usual expression for the cross section. In this appendix we report numerical results for some of these corrections for many of the states involved in HF. These values were calculated early in our work, simply to satisfy us that they were indeed negligible. The absolute numbers, therefore, come from a basis set that differs slightly from the final one. However, a comparison of the relative importance of the corrections should be meaningful.

The overlap contributions ( $\sum_n C_{n'n} S_n^{lj} \equiv \Delta_{n'}^{lj}$ ) are shown in Table V. The term ( $j = 1\sigma\beta$ ) obviously dominates all other  $j$ . Furthermore, since  $\langle \chi | \underline{p} | j \rangle \ll \langle \chi | \underline{p} | 1\sigma \rangle$  at x-ray energies, the entire second term in Eq. 17 can safely be disregarded. The conjugate factors ( $\sum_n C_{n'n} \left[ \prod_{\ell} \phi'_{\ell n} \left| \sum_{k=2}^N p_k \right| \Psi_i^{(N-1, \phi_j, 1)} \right] \equiv \Gamma_{n'}^{lj}$ ) are larger and somewhat less predictable. We estimate their importance as follows.

In the plane wave approximation for  $\chi$ , the term  $j = 1\sigma$  will affect the cross section as

$$\sigma_{n'} \propto \left| \underline{y} \cdot \left( \underline{k} \Delta_{n'}^{11} + \underline{\Gamma}_{n'}^{11} \right) \right|^2 \quad (6)$$

Since  $\underline{k}$  and  $\underline{\Gamma}$  are vectors, the "conjugate" correction will be angularly dependent. In the gas phase, one must average this expression over all possible orientations of the molecules with respect to  $\underline{y}$ , and for unpolarized x-rays, average over all polarizations. This leaves an expression which is dependent on the angle between the photoelectron

exit slit and the photon propagation direction. This angle in our instrument is  $\pi/2$ .

After performing these averages, one finds that the cross section is proportional to

$$\sigma_{n'} \propto (\Delta_{n'}^{11})^2 + \frac{2}{3k^2} (\Gamma_{n'}^{11})^2 \quad (7)$$

Although  $\Gamma_{n'}^{11}$  can sometimes be comparable to  $\Delta_{n'}^{11}$  (see Table V), the factor  $1/k^2$  effectively quenches this contribution well above threshold. The other terms ( $\Gamma_{n'}^{1j}$ ,  $j \neq 1\sigma$ ) are also negligible since they enter the expression multiplied by a smaller overlap integral  $\langle \chi | j \rangle$ .

We conclude that well above threshold only the first term of (Eq. I.17) should be necessary for the calculation of photoionization cross sections for core levels. As threshold is approached, the conjugate mechanism may become more important due to the presence of the  $1/k^2$  multiplicative factor.

FOOTNOTE AND REFERENCES

\* Work performed under the auspices of the Atomic Energy Commission.

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3. For further details see: D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.* 94, 6565 (1972).
4. The reason the energies are consistently higher than experiment is that the orbital basis used in the CI expansion was optimized for the primary hole state, not the correlation states.
5. All the computations described were performed using the experimental internuclear distance in HF (1.7328 a.u.). See Tables of Inter-atomic Distances and Configurations in Molecules and Ions, edited by L. E. Sutton (Chemical Society, London, 1958).
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7. C. F. Bender and E. R. Davidson, *J. Phys. Chem.* 70, 2675 (1966).
8. The configurations were found by diagonalizing the operator  $S^2 + \frac{1}{2} \sigma_v$  in the space defined by all possible Slater determinants which can be constructed from the orbital occupancy which have  $M_s = \sum_i (m_s)_i = \frac{1}{2}$  and  $\Lambda = \sum_i \lambda_i = 0$ . See H. F. Schaefer, *J. Comp. Phys.* 6, 142 (1970). The explicit expansion in Slater determinants for a few of the interesting cases is shown in the footnotes to Table IV.
9. This approach does not necessarily imply that our description of the excited states is better than a single configuration wavefunction.

The optimum spin-orbitals to construct such a configuration, however, are very difficult to obtain, and this configuration expansion is simply a relatively easy approach to generating the necessary excited state wavefunctions. The important thing this model allows for is the mixing of the various  $^2\Sigma^+$  final states which can be reached in terms of both  $\sigma \rightarrow \sigma$  and  $\pi \rightarrow \pi$  excitations.

10. C. F. Bender and H. F. Schaefer III, J. Chem. Phys. 55, 4798 (1971).
11. It should be noted that our utilization of the configuration-interaction technique was not aimed at obtaining an energetically superior wavefunction for the ground state; i.e., it was not an attempt to describe those correlation effects which contribute strongly to the total molecular energy. We hoped, however, to describe those components of the wavefunction not present in a single determinant which would be most important in terms of the transition moment to the final ionic states.
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Table I. Correlation Peak Intensities in the Overlap Approximation

State <sup>(a)</sup>	$(S_n^{11})^2$ <sup>(b)</sup> Method A	$(S_n^{11})^2$ <sup>(b)</sup> Method B	I(expt) <sup>(c)</sup>	FWHM (eV)	E(theo) <sup>(d)</sup> (eV)	E(expt) <sup>(d)</sup> (eV)
0	(1.000)	(1.000)	(1.000)	1.4	(693.5)	694.0(5)
1	0.000	0.001	—	—	23.89	—
2	0.012	0.020	0.019(3)	2.1(3)	25.90	22.4(2)
3	0.015	0.030	0.030(4)	2.3(3)	29.57	26.50(9)
4	0.000	0.000	—	—	30.89	—
5	0.036	0.062	0.057(5)	3.7(3)	32.35	29.90(7)
6	0.000	0.001	—	—	32.72	—
7	0.007	0.012	0.010	4.7(3)	33.31	30.87
8	0.000	0.000	—	—	33.74	—
9	0.028	0.041	0.038(5)	7.1(9)	34.84	32.7(3)
10	0.005	0.007	0.007	7.9(9)	35.43	33.3
11	0.000	0.000	—	—	35.72	—

a) In order of increasing energy "Reference state" is numbered 0, as in Fig. 1 and text.

b) All intensities normalized to peak 0. Absolute values of  $(S_0^{11})^2$  are 0.78115 (Method A), 0.71970 (Method B).

c) Error in last place given parenthetically.

d) First entry is the absolute binding energy of the reference state; the others are incremental energies relative to this.



Table II. Energy Dependence of Correlation Peak Cross Sections

State <sup>(a)</sup>	Q(E) <sup>(b)</sup> (dipole)	Q(E) <sup>(b)</sup> (sudden)	I(theo) <sup>(c)</sup> (dipole)	I(theo) <sup>(c)</sup> (sudden)
0	1.0	1.0	1.0	1.0
1	0.980	1.011	0.001	0.001
2	0.979	1.012	0.020	0.020
3	0.976	1.012	0.029	0.030
4	0.975	1.014	0.000	0.000
5	0.973	1.015	0.060	0.063
6	0.973	1.015	0.001	0.001
7	0.973	1.015	0.012	0.012
8	0.972	1.016	0.000	0.000
9	0.972	1.016	0.040	0.041
10	0.971	1.017	0.007	0.007
11	0.971	1.017	0.000	0.000

a) In order of increasing energy; state 0 is the "reference state".

b) Normalized to state 0.

c) Computed as the product of the energy dependent term, Q(E), and the overlap term for our best wavefunctions (Method B in Table I).

Table III. Basis Set of Slater Functions and Selected One-Electron Orbitals used in the CI Wavefunctions

A. HF Ground State													
Slater Function <sup>a</sup>		Molecular Orbitals											
Type	$\zeta$	1 $\sigma$	2 $\sigma$	3 $\sigma$	4 $\sigma$	5 $\sigma$	6 $\sigma$	7 $\sigma$	1 $\pi$	2 $\pi$	3 $\pi$	4 $\pi$	
1.	F(1s)	7.716	-0.6768	0.2873	0.0665	-0.0729	0.1185	0.0143	-0.0384				
2.	F(1s')	10.514	-0.3313	-0.0154	-0.0031	-0.0054	-0.0250	0.0088	0.0039				
3.	F(2s)	1.933	-0.0034	-0.4249	-0.1301	0.4412	0.1233	-0.2966	0.1057				
4.	F(2s')	3.120	0.0021	-0.6228	-0.1699	0.2847	-0.2811	-0.1380	0.1436				
5.	F(2p)	1.847	0.0005	-0.0885	0.6050	0.4963	0.2023	-0.0010	0.0957	-0.7149	-0.2956	-0.0323	0.1401
6.	F(2p')	4.175	-0.0012	-0.0266	0.2852	0.3050	0.1327	0.0056	0.0509	-0.3386	-0.2534	-0.0143	0.0958
7.	F(3d)	2.500	0.0001	-0.0216	0.0453	-0.0232	-0.0300	0.0878	0.0201	-0.0263	0.0116	-0.0552	-0.0003
8.	F(3s)	1.000	-0.0001	-0.0417	-0.0024	-0.2278	1.1467	-0.6601	-0.0954				
9.	F(3p)	1.000	-0.0009	-0.0193	0.0238	0.0163	-0.2236	-1.1454	-0.0880	-0.0600	1.0928	0.1275	-0.7086
10.	F(3d')	0.800	-0.0002	-0.0080	0.0134	0.0244	-0.1275	0.1289	0.6961	-0.0157	0.1735	-0.9572	0.1114
11.	F(4s)	0.600	-0.0001	0.0051	0.0036	-0.0292	-0.0576	-0.1121	0.7936				
12.	F(4p)	0.600	0.0002	-0.0016	0.0015	0.0245	0.0023	-0.2400	0.3504	0.0089	-0.0814	0.1208	1.2224
13.	H(1s)	1.000	0.0028	0.1841	-0.0297	-1.7194	-0.5649	1.5561	-0.7593				
14.	H(1s')	1.500	-0.0018	-0.2311	0.3042	0.3169	0.0954	-0.3849	0.3402				

B. HF <sup>+</sup> , F(1s) Hole State													
Slater Function		Molecular Orbitals											
Type	$\zeta$	1 $\sigma$	2 $\sigma$	3 $\sigma$	4 $\sigma$	5 $\sigma$	6 $\sigma$	7 $\sigma$	1 $\pi$	2 $\pi$	3 $\pi$	4 $\pi$	
1.	F(1s)	7.716	-0.5892	0.3055	0.0909	-0.0403	0.0588	-0.0087	0.0258				
2.	F(1s')	10.514	-0.4178	0.0035	-0.0038	-0.0125	-0.0177	-0.0119	-0.0024				
3.	F(2s)	1.933	-0.0305	-0.2378	-0.0022	0.5674	0.1979	0.3954	-0.0922				
4.	F(2s')	3.120	0.0071	-0.8100	-0.2620	0.1700	-0.0562	0.1087	-0.0539				
5.	F(2p)	1.847	-0.0005	-0.1273	0.5742	0.4799	0.2672	0.0312	-0.0984	0.6168	0.2489	0.0288	0.2153
6.	F(2p')	4.175	0.0005	-0.0714	0.4383	0.1111	0.0615	0.0153	-0.0147	0.4970	0.0996	0.0046	0.0638
7.	F(3d)	2.500	-0.0008	-0.0252	0.0474	0.0057	-0.0168	-0.0349	-0.0062	0.0282	-0.0067	0.0159	-0.0035
8.	F(3s)	1.000	-0.0023	-0.0435	0.0635	0.0661	1.3143	0.4695	0.4924				
9.	F(3p)	1.000	-0.0065	-0.0111	-0.0084	0.0563	0.1808	1.0704	0.3730	-0.0571	-0.9613	-0.1002	-0.9615
10.	F(3d')	0.800	-0.0022	-0.0073	0.0192	-0.0409	-0.1653	0.1510	-0.5887	0.0051	-0.2936	0.9282	0.2020
11.	F(4s)	0.600	-0.0007	0.0062	-0.0079	-0.0189	0.0819	0.1583	-0.9247				
12.	F(4p)	0.600	0.0011	-0.0046	0.0145	-0.0146	-0.0501	0.4501	-0.1900	0.0201	-0.1271	-0.2970	1.1986
13.	H(1s)	1.000	0.0238	0.1929	-0.2628	-1.7866	-1.3668	-1.7129	0.1798				
14.	H(1s')	1.500	-0.0134	-0.2196	0.3289	0.3656	0.3365	0.4841	-0.1434				

a) Here  $\psi \propto r^{n-1} e^{-\zeta r}$ , where n is the principal quantum number.

Table IV. Important Configurations for Describing the Correlation States

Configuration *		State											
		0	1	2	3	4	5	6	7	8	9	10	11
1.	$1\sigma^1 2\sigma^2 3\sigma^2 4\pi^4$ (a)	0.9957	0.0317	0.0170	0.0224	-0.0269	0.0118	-0.0014	-0.0164	-0.0052	-0.0013	0.0027	0.0084
2.	$1\sigma^1 2\sigma^2 3\sigma^1 4\sigma^1 4\pi^4$ (b)	-0.0075	0.6215	-0.7227	0.1656	-0.0181	-0.1269	0.0319	0.0395	0.0487	-0.1340	0.0191	0.0123
	(c)	0.0229	-0.7494	-0.5950	0.1153	-0.0865	-0.0707	0.0371	-0.0597	0.0264	-0.0362	0.0182	-0.0162
3.	$1\sigma^1 2\sigma^2 3\sigma^1 5\sigma^1 1\pi^4$ (b)	-0.0055	-0.0095	0.1233	-0.2445	-0.7273	-0.2901	0.1297	0.2317	0.3651	-0.2458	0.0770	0.0405
	(c)	0.0161	-0.0759	-0.0342	-0.0440	0.2883	0.2912	-0.1350	0.7881	0.0640	-0.1951	0.1067	0.0930
4.	$1\sigma^1 2\sigma^2 3\sigma^1 6\sigma^1 1\pi^4$ (b)	0.0011	-0.0065	0.0188	0.0402	0.2482	0.1689	-0.1184	-0.3500	0.8056	0.0648	0.1219	0.0517
	(c)	-0.0029	-0.0209	-0.0121	0.0204	-0.0820	-0.0801	0.0208	-0.1628	-0.3110	0.1045	-0.0068	0.0300
5.	$1\sigma^1 2\sigma^2 3\sigma^1 7\sigma^1 1\pi^4$ (b)	0.0007	-0.0172	0.0319	0.0204	0.0508	0.0037	-0.0280	-0.0394	0.0729	-0.3003	-0.9030	0.1157
	(c)	-0.0021	0.0276	0.0307	-0.0042	-0.0092	-0.0150	0.0014	-0.0257	0.0516	0.0688	0.2043	-0.0270
6.	$1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 2\pi^4$ (d)	-0.0148	-0.0469	0.2702	0.8815	0.0001	-0.2825	0.0561	0.1141	0.0410	-0.1243	0.0666	-0.0032
	(e)	0.0242	-0.0478	0.0567	-0.3138	0.5126	-0.7284	0.1145	-0.0098	-0.0096	-0.2211	0.1032	0.0081
7.	$1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 3\pi^4$ (d)	-0.0010	-0.0026	-0.0134	-0.0057	-0.1160	-0.2392	-0.9600	-0.0082	-0.0430	0.0159	0.0003	-0.0418
	(e)	0.0017	0.0099	-0.0010	-0.0092	0.0163	0.0098	0.0308	0.0767	0.0833	-0.0283	-0.1048	-0.9794
8.	$1\sigma^1 2\sigma^2 3\sigma^2 1\pi^3 4\pi^4$ (d)	-0.0092	-0.0165	0.0660	-0.0393	-0.0167	0.3076	-0.0726	-0.3383	-0.2199	-0.7779	0.2492	-0.0520
	(e)	0.0151	-0.0164	0.0203	-0.0806	0.0851	-0.0030	0.0056	0.0115	0.0180	0.1319	-0.1118	-0.0341

\*The configurations have the following specific forms.

a.  $1.0 (1\sigma\alpha 2\sigma\alpha 2\sigma\beta 3\sigma\alpha 3\sigma\beta 1\pi_+\alpha 1\pi_+\beta 1\pi_-\alpha 1\pi_-\beta)$

b.  $0.7990 (1\sigma\alpha m\sigma\alpha n\sigma\beta) - 0.5453 (1\sigma\alpha m\sigma\beta n\sigma\alpha) - 0.2537 (1\sigma\beta m\sigma\alpha n\sigma\alpha)$

c.  $-0.1683 (1\sigma\alpha m\sigma\alpha n\sigma\beta) - 0.6078 (1\sigma\alpha m\sigma\beta n\sigma\alpha) + 0.7761 (1\sigma\beta m\sigma\alpha n\sigma\alpha)$

d.  $0.5773 (1\sigma\alpha 1\pi_-\alpha m\pi_-\beta) - 0.2845 (1\sigma\alpha 1\pi_-\beta m\pi_-\alpha) + 0.5773 (1\sigma\alpha 1\pi_+\alpha m\pi_+\beta) - 0.2845 (1\sigma\alpha 1\pi_+\beta m\pi_+\alpha) - 0.2929 (1\sigma\beta 1\pi_-\alpha m\pi_-\alpha) - 0.2929 (1\sigma\beta 1\pi_+\alpha m\pi_+\alpha)$

e.  $0.0049 (1\sigma\alpha 1\pi_-\alpha m\pi_-\beta) - 0.5024 (1\sigma\alpha 1\pi_-\beta m\pi_-\alpha) + 0.0049 (1\sigma\alpha 1\pi_+\alpha m\pi_+\beta) - 0.5024 (1\sigma\alpha 1\pi_+\beta m\pi_+\alpha) + 0.4975 (1\sigma\beta 1\pi_-\alpha m\pi_-\alpha) + 0.4975 (1\sigma\beta 1\pi_+\alpha m\pi_+\alpha)$

Table V. Comparison of Overlap and Conjugate Terms in Photoemission Cross Sections for HF<sup>a,b</sup>

n'	j = 1σ β		j = 2σ β		j = 3σ β		j = 1π <sup>c</sup>
	$\Delta_{n'}^{1j}$	$\Gamma_{n'}^{1j}$	$\Delta_{n'}^{1j}$	$\Gamma_{n'}^{1j}$	$\Delta_{n'}^{1j}$	$\Gamma_{n'}^{1j}$	$\Gamma_{n'}^{1j}$
0	0.885	0.091	-0.006	-0.138	-0.001	-	-1.84
1	-0.014	0.192	0.001	-	-0.006	-	-
2	0.104	-0.454	0.000	-	0.001	-	-
3	-0.111	0.190	0.001	-	-0.003	-	-
4	-0.002	0.075	-0.000	-	-0.002	-	-
5	-0.178	0.082	0.000	0.085	0.001	-0.019	0.700
6	0.007	0.335	-0.000	-	0.000	-	-
7	0.083	0.178	-0.000	-	0.000	-	-
8	-0.051	0.273	0.000	-	-0.002	-	-
9	-0.018	-0.258	0.000	-	-0.000	-	-
10	-0.034	-0.034	0.000	-	-0.003	-	-

- See Appendix I for definitions of  $\Delta_{n'}^{1j}$  and  $\Gamma_{n'}^{1j}$ . The units for  $\Gamma_{n'}^{1j}$  are reciprocal bohrs.
- The dashes represent calculations which were not performed.
- Note that  $\Delta_{n'}^{1j}$  for j = 1π vanishes in all states by symmetry.

FIGURE CAPTIONS

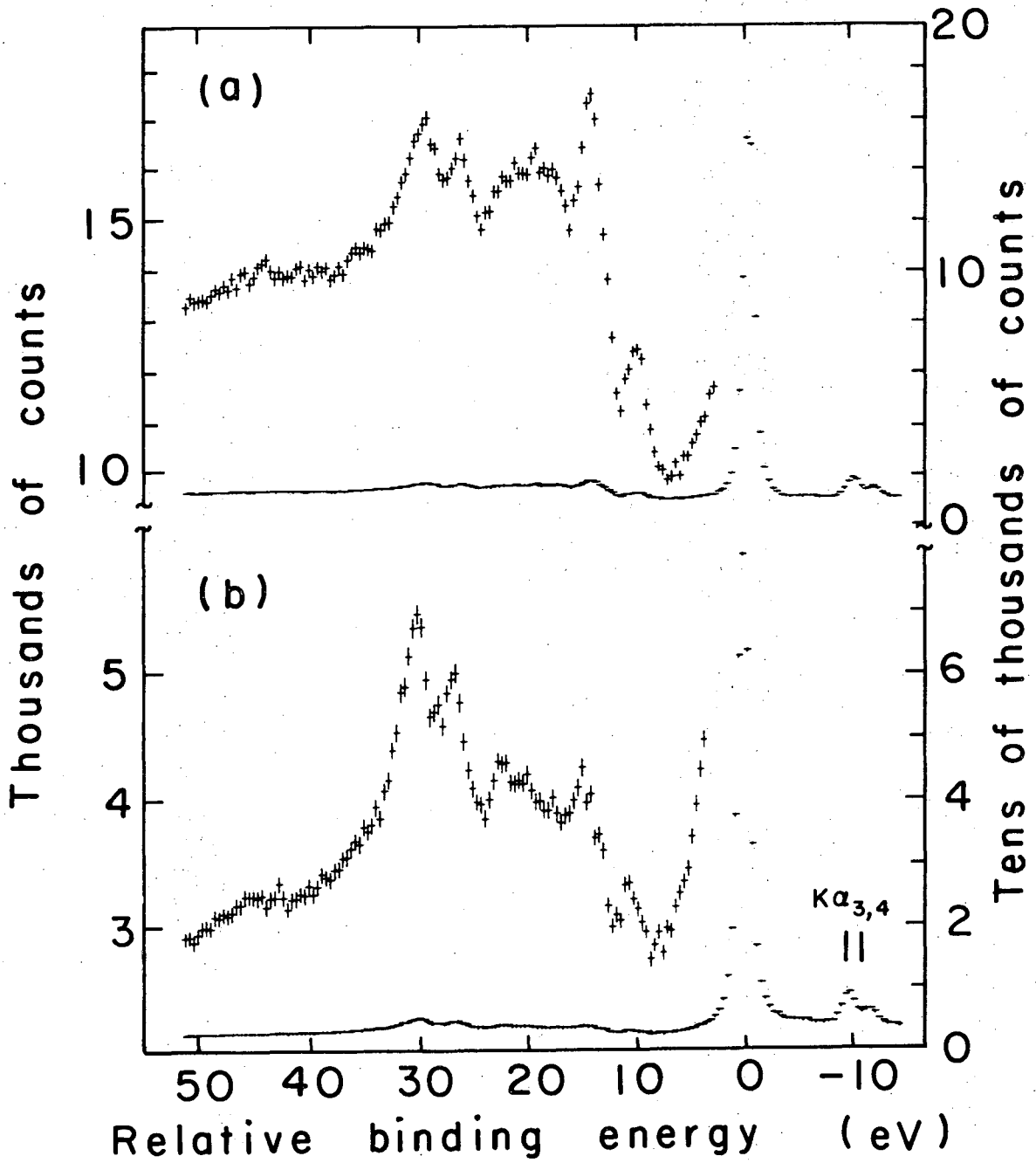
Fig. 1. a) High pressure and b) low-pressure photoelectron spectra of the F 1s region in HF using Al K $\alpha_{1,2}$  x-rays. The scale for the correlation and inelastic loss peaks is expanded 20 times that for the main peak.

Fig. 2. Correlation peaks of HF F 1s relative to the main line along with the computer fit (see Table I and text). The crosses represent actual data points; the circles represent data corrected for the inelastic energy loss peak at about 20 eV.

Fig. 3. a) The most intense satellites of the Ne 1s hole state. The correlation of these states with the HF satellites is shown by the dotted lines.

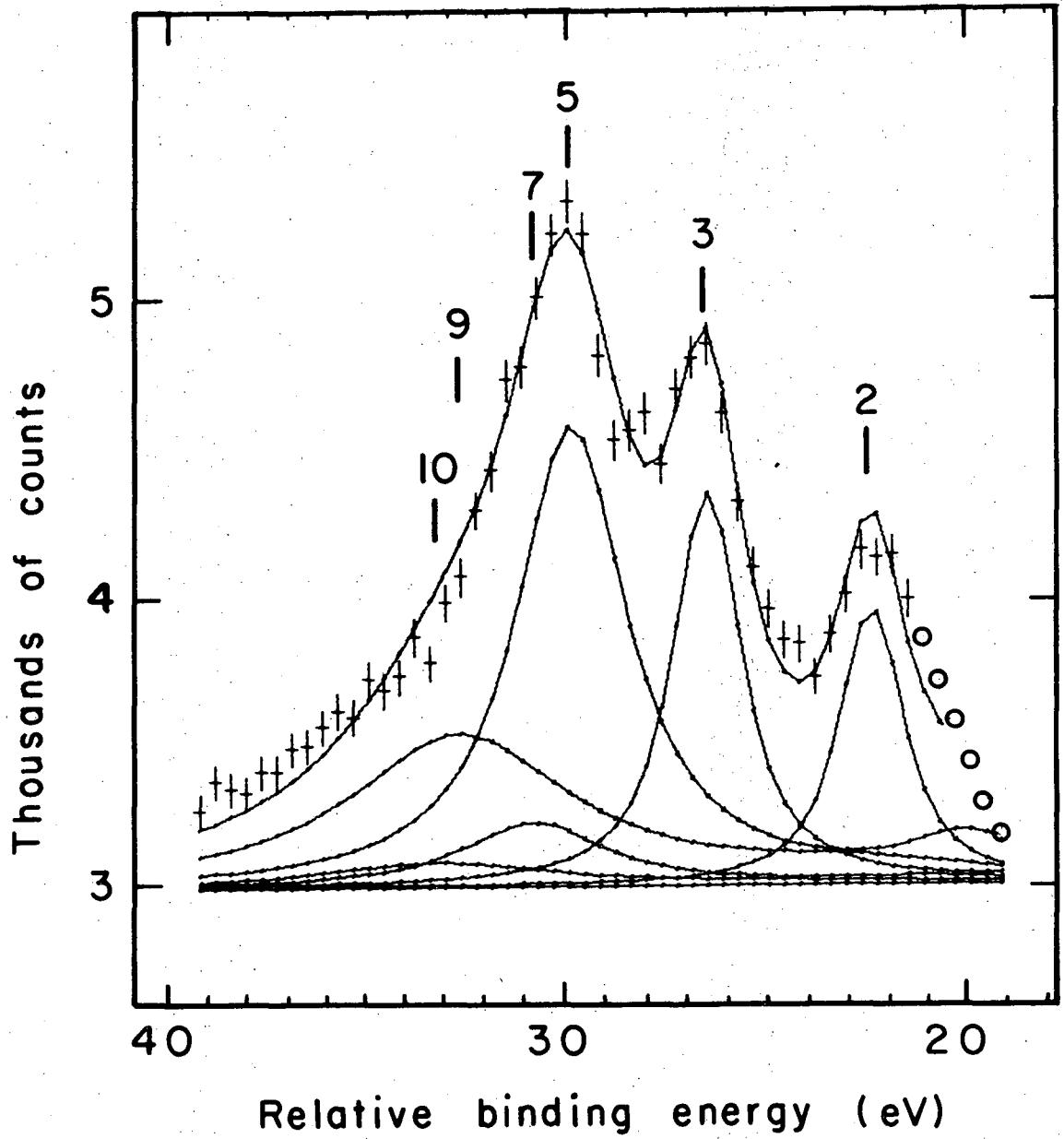
b) The most intense states of the HF satellite spectrum. The abscissa is the separation from the primary state and the ordinate is the intensity relative to the primary state. Above each bar an orbital designation is provided which roughly identifies the final state (see text).

c) The excited states derived from the configuration  $1s^2 2s^2 2p^4 3p$  of the Ne<sup>+</sup> ion. They have been given intensities based on the total degeneracy of each state.



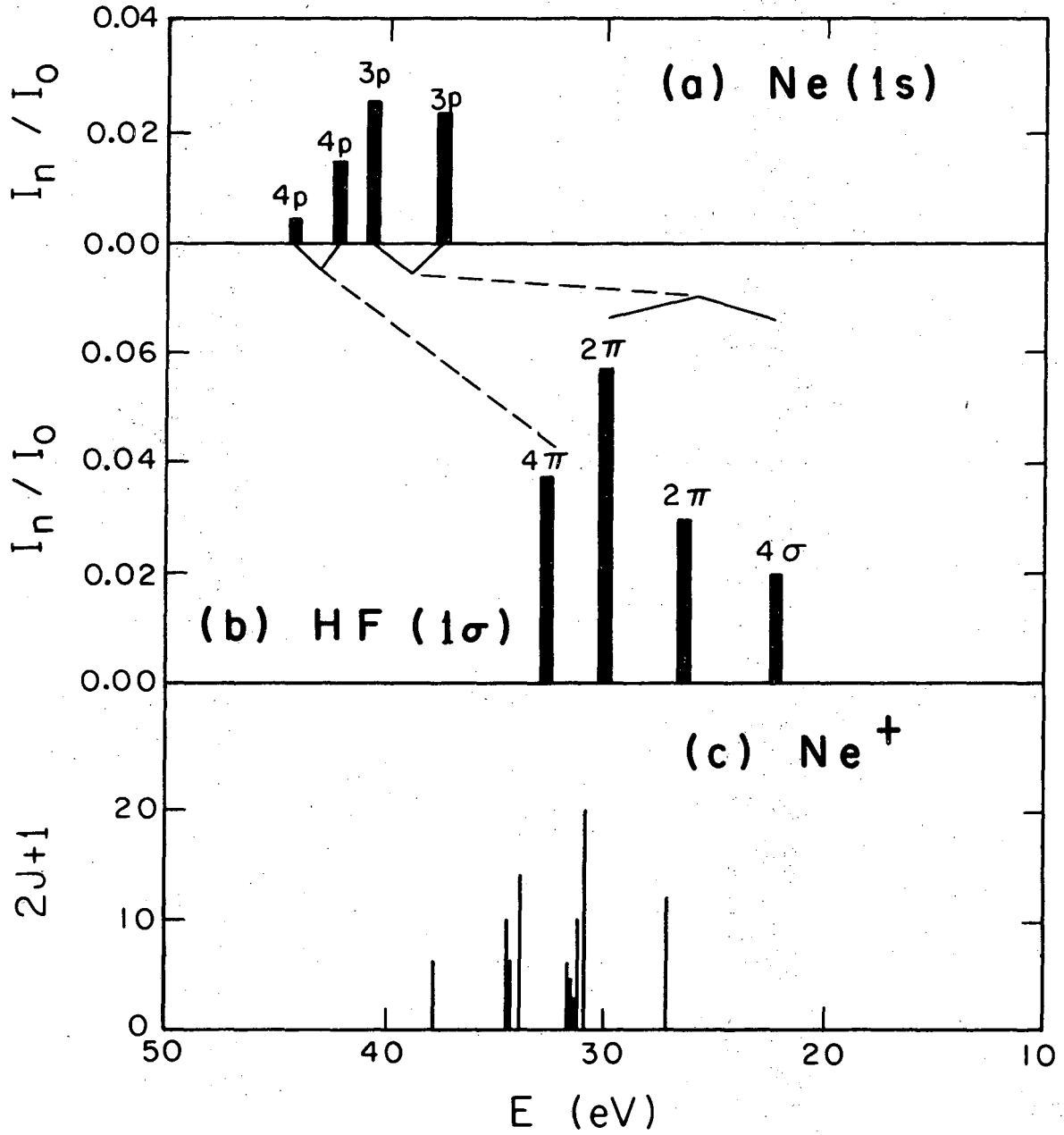
XBL 752-166

Fig. 1



XBL 7412-8360

Fig. 2



XBL752-2269

Fig. 3



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