PHYSICAL REVIEW A VOLUME 11, NUMBER 5 MAY 1975

Auger electron spectrum and ionization potentials of the HF molecule

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(Received 1 October 1974; revised manuscript received 20 January 1975)

The Auger electron spectrum of HF in the gas phase has been measured and the peaks identified with the transitions to the expected final states in HF^{++}. The relative energies and intensities are quite similar to those for the Auger spectrum of the isoelectronic atom neon. The additional features appearing in the HF spectrum are explained in terms of perturbations to Ne^{++} or F^{+} by an adjacent proton. The ionization potentials of HF have been measured by photoelectron spectroscopy. The energy-loss spectrum for 710-eV electrons incident on HF has been determined and the peaks identified with the expected excited states in the HF molecule.

I. INTRODUCTION

Auger spectra for atoms are well known and well understood; the same is true for molecules in which the ejected electrons are all core electrons. Molecular Auger spectra involving the ejection of valence electrons, however, tend to be quite complex with the result that most have not been completely characterized.[1-3] For HF, however, the spectrum is sufficiently similar to that for the isoelectronic atom neon that a reasonably clear correspondence can be made between the lines of the Auger spectrum and the energy levels of the HF^{++} ion. We report here the measurement and analysis of the HF Auger spectrum; we believe that this is the first molecular Auger spectrum for which a detailed analysis has been possible.

In connection with these investigations we have measured the ionization potentials of HF and the energy-loss spectrum for 710-eV electrons in HF. These data are also reported here.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Gaseous monomeric HF was prepared by filling a small reservoir with vapor in equilibrium with liquid HF. After this system had been isolated from the primary source, the HF was allowed to expand into a larger reservoir, such that the pressure was less than $\frac{1}{3}$ atm. At equilibrium under these conditions, HF is 97% monomer.[4] The gas was slowly bled from the final reservoir to the sample cell of our spectrometer.

Auger spectra were excited by both photoionization, using aluminum K x rays, and by electron impact, using electrons of about 8 keV. Although photoionization provided a superior signal to background ratio, the much higher counting rates obtained with electron impact made this the preferred technique. We observed no differences between spectra excited in the two different ways.

The Auger electron kinetic energies were measured in our cylindrical-mirror electrostatic analyzer.[5] Calibration was based on well-known lines in the neon Auger and photoelectron spectra run simultaneously with the HF.[6] All energies were determined by least-squares fits of Gaussian or Voigt functions to the spectra. A typical spectrum is shown in Fig. 1 where it is compared with a schematic representation of the neon Auger spectrum reported by Siegbahn *et al.*[1] Separate runs were made on the low-intensity peaks at 596 and 625 eV to obtain improved data. The solid lines represent the least-squares fits.

The energies and widths [full width at half-maximum (FWHM)] for the various peaks are summarized in Table I together with assignments of each peak to states in the ion HF^{++}. The basis for these assignments is discussed below.

The measured linewidths in Table I are due to contributions from the spectrometer resolution, thermal broadening (which is negligible in these experiments), and the intrinsic widths of the initial and final states. The intrinsic widths depend, in turn, on the lifetimes of the hole states involved and on the manifold of vibrationally or dissociatively excited states in the initial and final ions; contributions from these sources are taken up in detail in Sec. IV.

We determine the effect of spectrometer resolution by measuring the width of the neon $1s$ photoelectron peak excited with aluminum K x rays. These electrons have a kinetic energy of 616 eV, which is in the midst of the various HF Auger energies. Correcting the measured width for contributions from the aluminum radiation and from the known lifetime for the neon $1s$ hole state

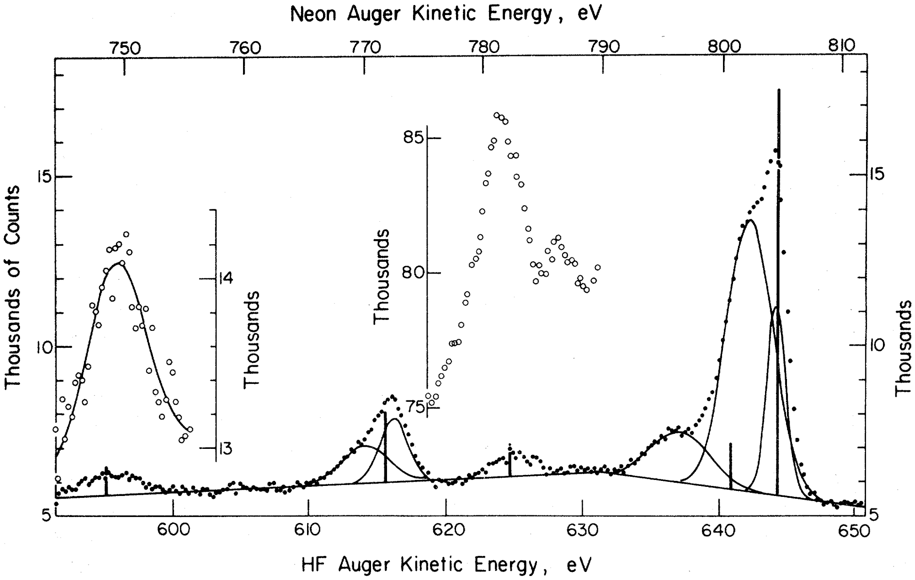

FIG. 1. Auger spectrum of HF. For the solid circles use the external scales. Open circles (internal scales) represent longer runs on the less-intense peaks. Solid lines are least-squares fits to the data. Vertical bars represent the neon Auger spectrum; note that the energy scale for neon (top) is different from that for HF.

(0.23 eV[7]), we conclude that the spectrometer resolution function at these energies is approximately Gaussian with a FWHM of 0.68 eV.

In the neon Auger spectrum there are many more peaks than we have shown in Fig. 1 or than we have observed for HF. Except for the $\mathrm{Ne}^{++}\ {}^3P$, these peaks are due to multiple vacancy states; their probabilities are correspondingly low and all have intensities of less than 5% of the main peak. The combination of low intensity, close spacing, and vibrational or dissociative broadening in the HF spectrum makes these less-pronounced features indistinguishable from the background.

III. INELASTIC SCATTERING OF ELECTRONS IN THE GAS

In order to determine whether peaks due to inelastic scattering of Auger electrons in the sample gas will interfere significantly with the identification of the Auger spectrum we have measured the energy-loss spectrum for 710-eV electrons in HF gas; the results of these measurements are shown in Fig. 2: We see from this spectrum that the major energy loss peaks are about 10–15 eV below the no-loss (elastic) peak. The contribution from this source to the Auger data may be estimated by convoluting the spectrum of Fig. 1 with that of Fig. 2. The rather broad Auger peaks around 642 eV will smear out the structure seen in Fig. 2 and give rise to a broad background at about 630 eV, as is observed.

TABLE I. Auger transitions in HF.

Configuration	Kinetic energy (eV)	Width (eV)
$(2\sigma^2)\ {}^1\Sigma$	595.6(1)	5.13(20)
$(2\sigma 3\sigma)\ {}^1\Sigma$	614.1(1)	4.10(25)
$(2\sigma 1\pi)\ {}^1\Pi$	616.2(1)	2.55(7)
$(2\sigma 3\sigma)\ {}^3\Sigma$ $(2\sigma 1\pi)\ {}^3\Pi$	625.1(1)	3.80(25)
$(3\sigma^2)\ {}^1\Sigma$	636.92(16)	4.50(22)
$(3\sigma 1\pi)\ {}^1\Pi$ $(1\pi^2)\ {}^1\Sigma$	642.35(8)	4.04(1)
$(1\pi^2)\ {}^1\Delta$	644.28(7)	1.62(3)
$(3\sigma 1\pi)\ {}^3\Pi$ $(1\pi^2)\ {}^3\Sigma$	Undetected	

The electronic states of HF have been only partially characterized. We may, however, tentatively identify all the observed peaks in the energy-loss spectrum. The first ionization potential of HF is 16.05 ± 0.04 eV,[8] and we see a peak in the energy-loss spectrum appearing above 16 eV with the characteristic shape of a transition into the

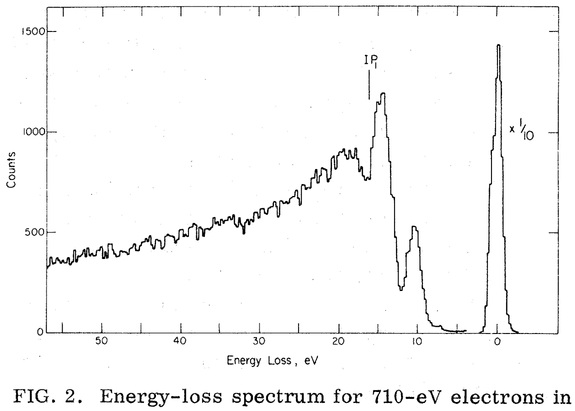

FIG. 2. Energy-loss spectrum for 710-eV electrons in HF. The position corresponding to the first ionization potential of HF is shown.

continuum. We assign the remaining peaks using the experimental studies of the emission and absorption spectra of HF by Di Lonardo and Douglas[9] and the calculations of the electronic states of the HF molecule by Bender and Davidson.[10] The peak at 11 eV is probably due to the vertical electronic transition from the HF $X\,{}^1\Sigma^+$ ground state to the first ${}^1\Pi$ excited state, which is repulsive. According to the calculations, the potential surface for this state at the internuclear distance of 1.733 bohrs (the HF ground-state bond length) lies at 10.98 eV above the minimum of the ground state, in good agreement with the observed energy. The most important component of the ${}^1\Pi$ state is a simple excitation of one of the π electrons to give the configuration $(2\sigma^2 3\sigma^2 1\pi^3 4\sigma)$.

Both the previous experimental work and calculations on the excited electronic states of HF indicate that the next transition that we expect to see in the electron energy-loss spectra is that to the $B\,{}^1\Sigma$ state. At the ground-state internuclear distance the $B\,{}^1\Sigma$ potential surface is at 13.99 eV (calculated). The work by Di Lonardo and Douglas and Bender and Davidson indicate that many other electronic states lie in this energy region so that the energy-loss spectrum is expected to be complex, and we see from Fig. 2 that a multiple peak does, in fact, appear in the energy-loss spectrum between 13 to 15 eV.

IV. DISCUSSION OF THE AUGER SPECTRUM

A. Assignments of peaks

We may use peak positions, widths, and intensities in the identification of the HF Auger spectrum. Considering first positions and intensities, we note that the Auger spectra for Ne and HF, shown in Fig. 1, are quite similar in both of these respects. The relative energy spacings of the main features of the two spectra are nearly identical. The relative intensities of the four major groups in the HF spectrum are (from left to right in Fig. 1) 0.054/0.18/0.050/1, almost identical to those for the corresponding groups in neon, 0.05/0.15/0.06/1. It seems reasonable, therefore, to view the HF spectrum as a neon spectrum with a "small" perturbation (due to the separation of a proton from the neon nucleus to an appropriate internuclear distance). The perturbation has two effects: (i) the transition energies are shifted to lower values and become more closely spaced but their order and relative spacing are unchanged; (ii) the neon $2p$ orbital is split into the 3σ and 1π molecular orbitals.

In the following we will identify states in the HF^{++} molecular ion according to the configuration of strongest parentage, i.e., we will neglect the effect of mixing of states originating from different parent states in Ne^{++}.

Let us first consider the excited state in the HF^{++} ion corresponding to the Auger transition of *lowest* kinetic energy. This is a ${}^1\Sigma$ state due to two vacancies in the 2σ molecular orbital; it corresponds to the ${}^1S$ state in Ne^{++} (due to two $2s$ vacancies).

The next two excited states in HF^{++} are due to the hole configurations $(2\sigma 3\sigma)$ and $(2\sigma 1\pi)$. These correspond to the vacancy state $(2s2p)\,{}^1P$ in the Ne^{++} parent which is split by the perturbation in HF. In agreement with this expectation, the next peak in the spectrum is composed of two peaks which we identify as $(2\sigma 3\sigma)\,{}^1\Sigma$ and $(2\sigma 1\pi)\,{}^1\Pi$. A peak with 10-eV-higher kinetic energy we attribute to the same configurations spin-coupled to the triplet states: ${}^3\Sigma$, ${}^3\Pi$. This peak is nearly symmetric and does not resolve unambiguously into two peaks. The spacing between the two triplet states appears to be significantly smaller than that between the corresponding singlet states.

The rather small peak appearing in the more detailed spectrum at 629 eV may be due to an Auger-satellite transition (two vacancies in the initial state).

The last group of peaks (about 640-eV kinetic energy) is rather complex. We believe it derives from the Ne^{++} parent hole states $(2p^2)\,{}^1D$ and $(2p^2)\,{}^1S$. The molecular perturbation will split the ${}^1D$ parent into three levels: $(1\pi^2)\,{}^1\Delta$, $(1\pi^2)\,{}^1\Sigma$, and $(1\pi 3\sigma)\,{}^1\Pi$. The ${}^1S$ parent in neon becomes $(3\sigma^2)\,{}^1\Sigma$ in HF. Now, however, we may no longer neglect mixing between states. The separation between the ${}^1D$ and ${}^1S$ states corresponding to $(2p^2)$ Ne^{++} is only 3.8 eV and hence we may expect significant mixing between the $(1\pi^2)\,{}^1\Sigma$ and $(3\sigma^2)\,{}^1\Sigma$ states in HF^{++}. A calculation described below suggests that, in order of decreasing excitation in the HF^{++} ion, the states are $(3\sigma^2)\,{}^1\Sigma$, $(3\sigma 1\pi)\,{}^1\Pi$, $(1\pi^2)\,{}^1\Sigma$, and $(1\pi^2)\,{}^1\Delta$ with the $(1\pi^2)\,{}^1\Sigma$ unresolved from the $(3\sigma 1\pi)\,{}^1\Pi$. Turning now to the spectrum in Fig. 1, we see that three peaks are indeed evident and we assign them to the ${}^1\Sigma$, ${}^1\Sigma$-${}^1\Pi$ (unresolved), and ${}^1\Delta$ states.

The energies and widths (full width at half-maximum) of these peaks, together with the assignments we have made, are summarized in Table I.

B. Linewidths

It is well known that loss of valence electrons that are strongly involved in chemical bonding leads to vibrational excitation or, in extreme cases, to dissociation.[11] The spectral lines associated with these events are broad in contrast with those due to loss of nonbonding electrons, which are narrow. In HF, the 2σ and 3σ electrons are expected to be bonding and the 1π to be nonbonding. Hence, we expect the linewidths of Auger transitions to depend on the vacancy configurations and to become increasingly broad as the number of σ electrons involved in the transition increases. Our assignments of the states in HF^{++} are in accord with these considerations. From the linewidths reported in Table I we see that those states resulting from the loss of two bonding electrons $[(2\sigma^2)\,^1\Sigma$, $(2\sigma3\sigma)\,^1\Sigma$, and $(3\sigma^2)\,^1\Sigma]$ are especially broad; the $(1\pi^2)\,^1\Delta$ state is quite narrow as expected. The states due to loss of one π and one σ electron $[(2\sigma1\pi)\,^1\Pi$ and $(2\sigma1\pi)\,^3\Pi]$ are intermediate in width. The states $(1\pi^2)\,^1\Sigma$ and $(3\sigma1\pi)\,^1\Pi$ are not resolved, and no experimental width information can be derived concerning them.

It remains to determine the relative importance of contributions to the observed linewidths from lifetime effects and from excitation of a manifold of states in the initial ion HF^+ and/or the final ion HF^{++}.

For most of the Auger transitions the contributions to the linewidth from initial- and final-state lifetimes are small. For the initial state the calculated lifetime of the fluorine $1s$ hole state corresponds to a width of 0.2 eV[12]; measurements we have made on x-ray photoelectron spectra of HF and other fluorine-containing compounds are in agreement with this result.[13] The excited HF^{++} ion may undergo another Auger (or Coster-Kronig) transition if it is sufficiently excited to be unbound with respect to loss of an electron. If the excitation energy in the HF^{++} ion (with respect to the HF^{++} ground state) is greater than the third ionization potential ($HF^{++} \rightarrow HF^{+++} + e$), decay by electron emission is energetically allowed. For example, the simple double-vacancy excitation states in Ne^{++} following *K-LL* Auger emission are all bound with respect to a second Auger transition. The situation is not so clear for HF for two reasons: (i) the $(1\pi^2)\,^3\Sigma$ transition leading to the HF^{++} ground state is too weak to be observed, hence we cannot determine accurately the absolute excitation energy of the observed HF^{++} states; (ii) the third ionization potential for HF is not known. We have estimated the energy difference between the $(1\pi^2)\,^3\Sigma$ and $(1\pi^2)\,^1\Delta$ states in HF^{++} and the third ionization potential of HF by comparison with the analogous values for neon; we find that the very highly excited $(2\sigma^2)\,^1\Sigma$ state in HF^{++} may be unbound with respect to electron emission to the ground state of HF^{+++} by as much as 5–10 eV. We believe, however, that even if it is energetically allowed, this transition would be very slow since a multiple electron transition would be required to fill both 2σ vacancies and eject a 1π electron.

The excited HF^{++} states can decay by photon emission but this process is relatively slow and its contribution to the observed linewidths is expected to be negligible.

Finally, we may expand earlier comments on the connection between the number of bonding electrons involved in the Auger transition and the Auger linewidths as follows. The population of vibrational levels in the initial state will be determined by Franck-Condon factors between the original neutral molecule and the ion with a core hole. From experiments on the x-ray photoelectron spectrum of HF, we have found that the envelope of these Franck-Condon factors can be approximately described by a Gaussian distribution with a FWHM of 0.6 eV.[13] If the vibrational spacing is large compared to the intrinsic width due to lifetime (approximately the case here), each state of HF^{*+} (HF^+ with a vacancy in the fluorine $1s$ shell) will decay independently to vibrational states of HF^{++}, with the relative populations being determined by appropriate Franck-Condon factors. The effect of the Auger transition from one distribution of vibrational states in HF^{*+} to another in HF^{++} on the Auger linewidth will depend on which of the following situations occurs. If each vibrational state of HF^{*+} decays to only one vibrational state in HF^{++}, then contributions to the width of the Auger line from the manifold of vibrational states may be quite small. If, on the other hand, each vibrational state of HF^{*+} decays to a manifold of vibrational states in HF^{++} there will be significant broadening from this source. Because each electronic state has a different molecular potential-energy surface, the amount of broadening will depend on which final electronic state is populated.

The latter of these two situations appears to be the case for HF. This is not surprising since one expects vibrational and dissociative broadening to accompany the extreme disruption of the valence electrons owing to the Auger process, especially those transitions involving 2σ or 3σ electrons. Even the ground-state HF^{++} ion is unstable for dissociation into H^+ and F^+ (^3P) by an estimated 10 eV.

C. Energies

The Auger energies in HF can be estimated by considering the perturbation produced in Ne^{++} by moving a proton from the neon nucleus to a radius of 1.733 a.u. (the proton-fluorine distance in HF, R_{HF}) or that produced in F^+ by bringing up a proton to the same distance from infinity.

We consider first the absolute Auger energies. These are equal to the difference between the energy of the initial state, with a core vacancy, and that of the final state, with two valence vacancies. In our approximation the initial state is F ($1s2s^2 2p^6$) plus a proton. Since the fluorine is neutral and the electron distribution is spherical, the energy is, to first order, unperturbed by the presence of the proton. The final state is F^+ (with two vacancies in the valence shell) and the proton. Ignoring, for the moment, the different possible orientations of p orbitals we see that the energy of the final state is higher by $e^2/R_{\rm HF}$ (=15.7 eV) than for an isolated F^+ ion. To a first approximation, then, the Auger energies in HF should be less than those produced following core ionization of F^- by about 16 eV. The actual differences are close to this, being typically 12–14 eV.[14]

For a more detailed consideration of the energies of the HF^{++} ion we must take into account the effects of both the perturbing proton and multiplet splitting, which are of comparable magnitude. As a basis set we take determinantal wave functions describing the two vacancies in the unperturbed isolated ion (F^+ or Ne^{++}). Appropriate linear combinations are taken so that the members of the basis set represent either singlets or triplets.

With certain exceptions, the proton affects only the diagonal matrix elements and, aside from the 16-eV over-all displacement mentioned above, only those in which there is a missing p electron. From wave functions[15] for p electrons on neon and fluorine we estimate the difference in energy between p_π and p_σ holes interacting with the proton to be about 3 eV with the p_π-hole configuration at lower energy. The perturbation due to the proton will give rise to off-diagonal matrix elements between configurations ($nl_m 2s$) and ($nl_m 2p_\sigma$) having the same spins. Since the states so-mixed differ in energy by 18–26 eV, we will ignore these off-diagonal elements.

The Coulomb interaction between the two holes gives rise to multiplet splitting. The matrix elements can be estimated from the known multiplet splitting in Ne^{++} and F^+. There are no off-diagonal elements between states of different symmetry; we assume that the only important off-diagonal elements are those between the two $^1\Sigma$ states resulting from the ($2p^2$) configuration.

The experimental energies are generally in accord with the results of these calculations. The $(2s^2)\,^1S$ state of Ne^{++} and F^+ is perturbed only by the over-all Coulomb displacement and becomes the $(2\sigma^2)\,^1\Sigma$ state of HF^{++}. The $(2s2p)\,^1P$ and ^3P states each are split into $(2\sigma 3\sigma)\,^1\Sigma$ and $^3\Sigma$ and $(2\sigma 1\pi)\,^1\Pi$ and $^3\Pi$. The splitting is the energy difference between the 3σ and 1π holes, estimated above to be about 3 eV. The experimental value is 2.1 for the singlet states; the triplets cannot be resolved. The singlet configurations resulting from (p^2), namely, ^1D and ^1S, become $(1\pi^2)\,^1\Delta$, $(1\pi^2)\,^1\Sigma$, $(3\sigma 1\pi)\,^1\Pi$, and $(3\sigma^2)\,^1\Sigma$, with energies (relative to $^1\Delta$) of 0, 1.8, 3.2, and 7.8 eV, respectively. We are unable to resolve the first $^1\Sigma$ and $^1\Pi$, but find a single broad peak at 1.9 eV away from the $^1\Delta$ peak. The second $^1\Sigma$ is found at 7.4 eV, in good agreement with the calculated value.

This simple calculation leads to the prediction that the $(2s2p)\,^3P$ and ^1P states in the Ne^{++} should be equally split by the addition of a proton. This is not the case, however; the singlet is split by 2.1 eV and the triplet is unresolvable. The failure of our model to account for this difference may be due to our neglect of some of the off-diagonal matrix elements.

Energies are among the least sensitive of molecular properties to the details of the charge distribution; because of this even our simple model has been reasonably successful in reproducing some of the features of the HF Auger electron spectrum.

The simplifications we have made in calculating energy differences between states are equivalent to assuming an ionic view of the HF^{++} system. We have neglected electron rearrangement and polarization of the fluorine atomic orbitals caused by the presence of the proton. The use of a more complete basis set and proper treatment of off-diagonal matrix elements neglected here would correct for these deficiencies. An interesting calculation of the total energy of the HF molecule has been carried out by Lee, Dutta, and Das.[16] Using many-body perturbation-theory approach, they treat HF as the united atom neon with the difference between the neon atomic and HF molecular potential as the perturbation. Their calculated total energy is in excellent agreement with the experimental value (if allowance is made for relativistic effects).

Our observation, that the HF Auger spectrum is very "neonlike" is not surprising. In the initial state, the fluorine 1s vacancy gives the fluorine core (fluorine nucleus and 1s electrons) the appearance of a neon core; hence the valence-electron orbitals are substantially contracted and the picture of a neon valence-electron cloud perturbed by a proton becomes a rather good approximation.

From this simplest case we may move to more complex but similar molecules. Moddeman *et al.*[2] and Siegbahn[17] have reported the H_2O Auger spectrum, which is similar in its over-all gross structure to that of neon. In the H_2O molecule all of the degeneracy remaining in HF is removed, nonetheless, the energies of the valence orbitals fall into the same two groups—those whose principal parentage is from the heavy atom $2p$ and $2s$, respectively. As a result the Auger spectrum exhibits three groups of peaks in order of decreasing kinetic energy: (1) those corresponding to the final state in which two vacancies remain in the first set of orbitals,[18] (2) those with one vacancy in the first set and one in the deepest-lying $(2a_1)$ orbital, and (3) those with two vacancies remaining in the $2a_1$ orbital. The over-all spectrum is quite similar to that for HF.

By comparing our HF Auger spectrum with the H_2O Auger spectrum we may make the following tentative assignments. The peak called D-1 by Moddeman *et al.*[2] is associated with the H_2O^{++} vacancy state $(2a_1^2)\,^1A_1$. The sharp peak labeled B-1 is principally due to $(1b_1^2)\,^1A$, and is analogous to the sharp peak in HF that we have assigned to $(1\pi^2)\,^1\Delta$. These assignments agree with those given by Moddeman *et al.* The peaks C-1 and C-2 are due to the $(1b_2 2a_1)\,^1B_2$, $(3a_1 2a_1)\,^1A_1$, and $(1b_1 2a_1)\,^1B_1$ states, and B-3 and B-4 are due to the corresponding triplets. The broad B-2 peak is an envelope containing the peaks associated with the following H_2O^{++} final states: $(1b_1 3a_1)\,^1B_1$, $(3a_1^2)\,^1A_1$, $(1b_1 1b_2)\,^1A_2$, $(3a_1 1b_2)\,^1B_2$, and $(1b_2^2)\,^1A_1$. These assignments are in essential agreement with the peak positions calculated by Siegbahn, with the possible exception of peak B-3, which, according to Siegbahn's calculation, corresponds to the $(1b_2^2)\,^1A$ configuration. This calculation, however, does not appear to take into account any splitting of the configurations into singlet and triplet states.

Because of the nature of many of the H_2O^{++} final states—highly vibrationally excited or dissociative—and mixing of states of the same symmetry, a closer identification of the H_2O Auger spectrum is probably very difficult. Even for the very simple HF case, the intrinsic width of the states causes severe overlapping of several of the peaks. Our observations suggest that, except for transitions to well-separated states in the final ion [$(2a_1^2)\,^1A_1$ state in H_2O^{++}, $(2\sigma^2)\,^1\Sigma$ state in HF^{++}], the Auger spectrum of molecules will not convey precise information concerning highly excited molecular ions.

V. IONIZATION POTENTIALS OF HF

During these experiments all of the ionization potentials of the HF molecule were measured; they are given in the second column in Table II. Each result is the mean of several measurements for each ionization potential. Absolute energy calibrations were determined by running the calibrant gas neon simultaneously with the HF or immediately after the HF measurements. The neon lines used were the $^1D_2$ Auger transitions at 804.557 ±0.017 eV[6] and the ^2S ionization potential at 48.47 eV.[19] The reported uncertainties include the standard deviation of the mean of the measurements and the absolute uncertainties of the calibration energies. Correction for recoil of the molecular ion has been made.

The third and fourth columns in Table II show the results by Banna *et al.*[20] and by Berkowitz,[21] respectively. The ionization-potential measurements by Banna *et al.* were made using Al K_α or Mg K_α x rays and their results agree well with ours. The work by Berkowitz was done using the He 584-Å and Ne 736-Å lines for excitation; transitions to individual vibrational levels in the HF^+ ion were resolved and the entries in Table II are for the $0 \rightarrow 0$ vibrational transition. The x-ray induced transitions to individual vibrational levels are not resolved in x-ray photoelectron spectroscopy and we expect a given line in the photoelectron spectrum to be due to an envelope over a range of vibrational states in the molecular ion. The average energy corresponds to the vertical ionization potential. The molecular constants of the $^2\Pi$ ground state and $^2\Sigma^+$ state in HF^+ have recently been determined by Gewurtz and Lew[22]; the values for R_e (Å) are 1.0013 and 1.2245, respectively. Comparing these values with the ground-state internuclear distance for the HF molecule (0.9171), we expect that the vertical ionization potentials measured by the x-ray experiment will be significantly higher than the first ionization potential measured in the uv experiment for the 3σ ionization and somewhat higher for the 1π ionization. A comparison of our values with those of Berkowitz in Table II shows that this is indeed the case.

ACKNOWLEDGMENTS

We thank Dr. Thomas Carroll for assistance in programming the peak-fitting routines and Dr. Mau Hsiung Chen for a stimulating discussion of Auger transitions. This work was supported in part by the U.S. Atomic Energy Commission.

TABLE II. HF ionization potentials (in eV).

Configuration	This work	X-ray photoelectron spectroscopy[a]	UV photoelectron spectroscopy[b]
1π	16.05(4)	16.12(4)	16.03(1)
3σ	19.82(5)	19.89(7)	19.118
2σ	39.58(2)	39.65(2)	
1σ	694.25(8)		

[a] Reference 20. [b] Reference 21.

[1] K. Siegbahn *et al.*, *ESCA* (Almqvist & Wiksell, Uppsala, 1967); *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[2] W. E. Moddeman, Ph.D. thesis (University of Tennessee, 1970) (unpublished). W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. 55, 2317 (1971).

[3] L. Karlsson, L. O. Werme, T. Bergmark, and K. Siegbahn, J. Electron. Spectrosc. 3, 181 (1974).

[4] J. N. Maclean, F. J. C. Rossotti, and H. S. Rossotti, J. Inorg. Nucl. Chem. 24, 1549 (1962).

[5] P. H. Citrin, R. W. Shaw, Jr., and T. D. Thomas, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 105.

[6] R. W. Shaw, Jr. and T. D. Thomas, J. Electron. Spectrosc. 5, 1081 (1974).

[7] U. Gelius, S. Svensson, H. Siegbahn, E. Basilier, Å. Faxälv, and K. Siegbahn, Chem. Phys. Lett. 28, 1 (1974).

[8] See Sec. V of this paper.

[9] G. Di Lonardo and A. E. Douglas, Can. J. Phys. 51, 434 (1973).

[10] C. F. Bender and E. R. Davidson, J. Chem. Phys. 49, 4989 (1968).

[11] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970).

[12] E. J. McGuire, Phys. Rev. 185, 1 (1969).

[13] R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas (unpublished).

[14] The Auger energies in F^- may be estimated from the energy of K x rays of F^- in ionic crystals (676.7 eV), the first ionization potential of F, and the known energy levels of F^+.

[15] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[16] T. Lee, N. C. Dutta, and T. P. Das, Phys. Rev. Lett. 25, 204 (1970).

[17] K. Siegbahn, J. Electron. Spectrosc. 5, 66 (1974).

[18] The molecular orbitals whose parentage is mainly from the oxygen $2p$ and hydrogen $1s$ are $1b_1$, $3a_1$, and $1b_2$ in order of increasing ionization potential. The oxygen $2s$ contributes principally to the $2a_1$ orbital.

[19] J. C. Boyce, Phys. Rev. 46, 378 (1934).

[20] M. S. Banna, B. E. Mills, D. W. Davis, and D. A. Shirley, J. Chem. Phys. 61, 4780 (1974).

[21] J. Berkowitz, Chem. Phys. Lett. 11, 21 (1971).

[22] S. Gewurtz, H. Lew, and P. Flainak, Can. J. Phys. (to be published).