

# Theoretical studies of molecular ions. Vertical ionization potentials of hydrogen fluoride

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The  ${}^2\Pi$  and  ${}^2\Sigma^+$  vertical ionization energies of hydrogen fluoride are studied within the framework of an equations-of-motion approach, which permits the direct calculation of the ion-molecule energy differences. The contributions of charge redistribution and correlation energy change to the calculated ionization potentials are evaluated. The computational efficiency of the method is illustrated and comparisons are made with recent photoionization experimental results.

## I. INTRODUCTION

In a previous publication,<sup>1</sup> hereafter referred to as (I), we developed a physically clear and computationally tractable theory of molecular electron affinities and ionization potentials. In our approach, the ion-molecule energy difference is obtained directly rather than as a result of carrying out two separate variational calculations. Such a direct-calculation theory permits us to effect a formal cancellation of those terms which contribute equally, through third order in perturbation theory, to the ion and molecule energies. Connections between our equations-of-motion (EOM) technique and Rayleigh-Schrödinger perturbation theory (RS) and a third-order approximation to the self-energy of Green's function theory have been discussed by us in (I) and elsewhere.<sup>2</sup> It is sufficient for understanding the results presented here to recall from (I) that the adjustment of the parent's Hartree-Fock molecular orbitals as well as the change in correlation energy which accompanies ionization are incorporated into our theory in a manner which allows the ion-molecule energy difference to be obtained accurately through third order in the electron interactions  $v_{ij}^{-1}$ .

A principal purpose of the present paper is to present and analyze the results of applying our EOM method to the  $X^1\Sigma^+ \rightarrow {}^2\Pi$  and  $X^1\Sigma^+ \rightarrow {}^2\Sigma^+$  vertical ionization energies of the hydrogen fluoride molecule.<sup>3</sup> The experimental data on this molecule, which was obtained by Berkowitz *et al.*,<sup>4</sup> provides us with an excellent source of information with which to compare our theoretical predictions. In Sec. II the computational methods used to obtain the ionization energies are described briefly. Section III contains the results of these initial test calculations as well as a discussion of their probable accuracy and some comments concerning our future research in this area.

## II. DESCRIPTION OF THE METHOD

In the EOM theory of electron affinities and ionization potentials derived in (I), the excitation operator  $\Omega_\mu$ , which generates the, in principle exact, eigenstate  $|\mu^+\rangle$  of the positive ion when operating on the true neutral-molecule ground state  $|g\rangle$ ,

$$\Omega_\mu |g\rangle = |\mu^+\rangle, \quad (1)$$

is approximated in terms of the second-quantized Hartree-Fock orbital creation  $\{C_i^\dagger\}$  and annihilation  $\{C_i\}$  operators as follows<sup>5</sup>:

$$\Omega_\mu = \sum_i X_i(\mu) C_i + \sum_{m < n, \alpha} Y_{n\alpha m}(\mu) C_n C_\alpha^\dagger C_m + \sum_{\alpha < \beta, m} Y_{\alpha m \beta}(\mu) C_\alpha C_m^\dagger C_\beta. \quad (2)$$

The operator  $C_i^\dagger(C_i)$  creates (destroys) an electron in the Hartree-Fock spin orbital  $\varphi_i$ . Greek indices  $\alpha, \beta, \gamma$  label "occupied" Hartree-Fock spin orbitals,  $m, n, p, q$  label "unoccupied" spin orbitals, and  $i, j, k, l$  label either set. The  $X_i(\mu)$ ,  $Y_{n\alpha m}(\mu)$ , and  $Y_{\alpha m \beta}(\mu)$  are expansion coefficients which are determined by making use of the EOM theory of (I) whose pertinent aspects are briefly reviewed below. An analogous expansion for the operator  $\Omega_\lambda^+$  which generates negative-ion eigenstates when operating on  $|g\rangle$  is also given in (I).

By assuming that  $|g\rangle$  and  $|\mu^+\rangle$  exactly obey the following Schrödinger equations

$$H|g\rangle = E|g\rangle, \quad (3a)$$

and

$$H|\mu^+\rangle = E_\mu^+|\mu^+\rangle, \quad (3b)$$

one immediately obtains the basic equations of motion

$$[H, \Omega_\mu]|g\rangle = (E_\mu^+ - E)\Omega_\mu|g\rangle \quad (3c)$$

which were used in (I) to derive the working matrix pseudoeigenvalue problem involving the electron affinities or ionization potentials and the coefficients  $X_i(\lambda)$ , or  $X_i(\mu)$

$$\sum_j H_{ij}(\Delta E_\lambda) X_j(\lambda) = \Delta E_\lambda X_i(\lambda), \quad (4a)$$

or

$$\sum_j H_{ij}(\Delta E_\mu) X_j(\mu) = \Delta E_\mu X_i(\mu), \quad (4b)$$

where  $\Delta E_\lambda$  is  $E_\lambda^- - E$  and  $\Delta E_\mu = E - E_\mu^+$ . These results can be derived by using the approximation to  $\Omega_\mu$  given in Eq. (2) or its electron-affinity analog and the RS approximation to  $|g\rangle$

$$|g_{RS}\rangle = N_0^{-1/2} \left\{ |0\rangle + \sum_{m < n, \alpha < \beta} \langle mn | \alpha\beta \rangle (\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n)^{-1} C_m^* C_n^* C_\beta C_\alpha |0\rangle \right\} \quad (5)$$

in Eq. (3c). The coefficients  $Y_{n\alpha m}$  and  $Y_{\alpha m\beta}$  have been eliminated by partitioning the resulting equations. In Eq. (5)  $N_0$  is a normalization constant,  $\epsilon_i$  is the Hartree-Fock energy of spin orbital  $\varphi_i$ , and the  $\langle mn | \alpha\beta \rangle$  are antisymmetrized two-electron integrals over the spin-orbitals  $\varphi_m, \varphi_n, \varphi_\alpha$ , and  $\varphi_\beta$ . The Hartree-Fock wavefunction of the neutral parent is represented by  $|0\rangle$ . The elements of the matrix  $H_{ij}(\Delta E)$  are given in Eq. (37) of (I) as

$$H_{ij}(\Delta E) = A_{ij} + \sum_{\alpha < \beta, m} \frac{B_{i, \alpha m\beta} B_{j, \alpha m\beta}^*}{E_{\alpha\beta}^m + \Delta E} + \sum_{m < n, \alpha} \frac{B_{i, n\alpha m} B_{j, n\alpha m}^*}{-E_{\alpha mn} + \Delta E}, \quad (I-37)$$

where  $\Delta E$  is either  $\Delta E_\lambda$  or  $\Delta E_\mu$  and the quantities appearing in this equation, which are defined in Eqs. (31d)–(35) of (I), are reproduced here for the sake of completeness.

$$A_{ij} = \delta_{ij} \epsilon_i + \sum_{k, l} \langle ik | jl \rangle F_{kl}, \quad (I-31d)$$

$$B_{i, \alpha m\beta} = -\langle im | \alpha\beta \rangle - \frac{1}{2} \sum_{p, q} \langle im | pq \rangle K_{\alpha\beta}^{pq} + \sum_{\gamma, \delta} [\langle i\gamma | p\alpha \rangle K_{\beta\gamma}^{mp} - \langle i\gamma | \beta\delta \rangle K_{\alpha\gamma}^{mp}], \quad (I-31e)$$

$$B_{i, n\alpha m} = \langle i\alpha | mn \rangle + \frac{1}{2} \sum_{\gamma, \delta} \langle i\alpha | \delta\gamma \rangle K_{\delta\gamma}^{mn} + \sum_{\gamma, \delta} [\langle i\delta | \gamma n \rangle K_{\alpha\gamma}^{mp} - \langle i\delta | \gamma m \rangle K_{\alpha\gamma}^{np}], \quad (I-31f)$$

$$F_{kl} = \sum_{\alpha < \beta, p} K_{\alpha\beta}^{pk} K_{\alpha\beta}^{pl} - \sum_{p < q, \alpha} K_{\alpha l}^{pq} K_{\alpha k}^{pq}, \quad (I-32)$$

$$E_{\alpha}^{mn} = \epsilon_m + \epsilon_n - \epsilon_\alpha - \langle \alpha m | \alpha m \rangle - \langle \alpha n | \alpha n \rangle + \langle mn | mn \rangle, \quad (I-34)$$

$$E_{\delta\gamma}^{p\delta} = \epsilon_p - \epsilon_\delta - \epsilon_\gamma - \langle \delta p | \delta p \rangle - \langle \gamma p | \gamma p \rangle + \langle \delta\gamma | \delta\gamma \rangle, \quad (I-35)$$

and

$$K_{\alpha\beta}^{pq} = \langle pq | \alpha\beta \rangle (\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)^{-1}. \quad (I-15)$$

Although the above quantities are rather complicated, it should be kept in mind that a knowledge of the orbital energies  $\{\epsilon_i\}$  and two-electron integrals  $\langle ij | kl \rangle$  is sufficient to permit the formation of  $H_{ij}(\Delta E)$ . The physical content of the terms in the above expression for  $H_{ij}(\Delta E)$ , which is discussed more completely in (I), can be summarized, for the case of ionization potentials, as follows:

(i) The  $\beta = N$  terms in the first sum in Eq. (I-37) contribute to the ion-neutral Hartree-Fock energy difference; therefore, these terms contain the effects of charge redistribution on the calculated ionization energies.

(ii) The second sum approximates the negative of the correlation energy of an electron in  $\varphi_N$ , which is vacant in the positive ion, interacting with all other electrons.

(iii) The  $\beta < N$  terms in the first sum give the approximate change in correlation energy of the parent's  $N$  electrons caused by the removal of an electron from  $\varphi_N$ .

To make use of Eq. (4a) or Eq. (4b), one must first carry out a Hartree-Fock calculation on the parent molecule of interest, after which the necessary<sup>6</sup> two-electron integrals must be transformed to the Hartree-Fock basis. In its present form, the theory is restricted, because<sup>7</sup> of the use of Eq. (5) for  $|g\rangle$ , to closed-shell parent molecules. This does not prohibit us from computing the electron affinity of, for example, the OH radical, however, because we can obtain the desired energy difference by calculating the ionization potential of the closed-shell species  $\text{OH}^-$ . Only those energy differences for which neither the ion nor the molecule are closed shell are presently outside the capability of our method. We are currently devoting considerable effort toward developing an extension of our EOM approach for use on such open-shell systems.

Once the Hartree-Fock orbital energies and two-electron integrals have been computed, the quantities  $A_{ij}$ ,  $E_{\alpha}^{mn}$ ,  $E_{\alpha\beta}^m$ ,  $B_{i, n\alpha m}$ ,  $B_{j, n\alpha m}$ , and  $B_{i, \alpha m\beta}$ ,  $B_{j, \alpha m\beta}$ , which are defined in Eqs. (I-31d)–(I-35), can be formed. This step is carried out only once; it is not part of the iterative procedure used to solve Eq. (4a) or Eq. (4b) which is described below. The fact that  $\mathbf{H}(\Delta E)$  is block diagonalized by molecular symmetry allows us to compute only a limited set of the above-mentioned quantities, which leads to a very important savings in computation quantities. As an initial approximation to the desired ionization potential  $\Delta E_\mu$  or electron affinity  $\Delta E_\lambda$ , one can choose the Koopman's theorem<sup>8</sup> value

$$\Delta E \cong \epsilon_i, \quad (6)$$

for ionization from (or into) orbital  $\varphi_i$ . In this approximation, we assume that the state of the ion being studied is related, through zeroth order, to the parent's Hartree-Fock wavefunction by the addition or removal of an electron from a single spin orbital. For the so-called shake up states<sup>9</sup> of a positive-ion, in which ionization is accompanied by excitation of the ion, the initial estimate for  $\Delta E_\mu$  should be taken to be of the form  $\epsilon_\alpha + \epsilon_\beta - \epsilon_p$ , where the meaning of the subscripts was discussed earlier. Such states are not treated in our studies of hydrogen fluoride and will not be discussed further here. The fact that the Koopman's theorem initial guess may be quite far ( $\geq 1$  eV) from the correct  $\Delta E$  leads one to inquire about the possibility of the iterative procedure

TABLE I. Seventeen-function Hartree-Fock wavefunction for HF.  $R=1.7328$  a.u.,  $E=-100.0236$  a.u.,  $\epsilon_{1\sigma}=-26.3187$ ,  $\epsilon_{2\sigma}=-16.1651$ ,  $\epsilon_{3\sigma}=-0.7680$ ,  $\epsilon_{1\pi}=-0.6627$ .

$\sigma$ atomic orbitals	$1\sigma$	$2\sigma$	$3\sigma$	$\pi$ atomic orbitals	$1\pi$
F1s (7.9437)	0.9098	-0.2286	-0.0663	F2p (1.3584)	0.3395
F2s (1.9346)	0.0227	0.4607	0.2311	F2p' (2.3291)	0.4608
F2p (1.4070)	-0.0086	-0.0124	0.2258	F2p'' (4.2614)	0.2322
F1s' (14.1095)	0.1079	0.0158	0.0016	H2p (1.7706)	0.0444
F2s' (3.2563)	-0.0273	0.5674	0.1362		
F2p' (2.3732)	0.0069	-0.0956	0.4188		
F2p'' (4.2784)	-0.0037	-0.0156	0.2210		
H1s (1.3727)	-0.0127	0.0593	-0.3590		
H1s (2.4605)	0.0066	0.0547	-0.0034		

converging to some ion-molecule energy difference other than the energy which is appropriate to the state of interest. Because the pseudoeigenvalue problem expressed in Eq. (4a) or Eq. (4b) is symmetry diagonalized, this problem will arise only if there exists a state whose symmetry is the same as that of the state of interest and whose ionization energy is close to the initial Koopmans' theorem estimate. In this uncommon situation, a more detailed analysis of the dependence of the solution to Eq. (4a) or Eq. (4b) upon the initial estimate for  $\Delta E$  is required; in all of our calculations to date, such difficulties have not arisen.

Given the quantities appearing in Eqs. (I-31d)-(I-35) and an initial approximation to  $\Delta E$ , the matrix elements  $H_{ij}(\Delta E)$  belonging to the proper symmetry block can be formed in a straightforward manner, as shown in Eq. (I-37).<sup>10</sup> The particular eigenvalue of  $\mathbf{H}(\Delta E)$  which lies closest to the previous approximation to  $\Delta E$  can then be used as the next approximation in forming a new  $\mathbf{H}(\Delta E)$  matrix. This iterative solution of the working equations [Eq. (4a) or (4b)] of our theory, in combination with Aiken's method<sup>11</sup> for improving the rate of convergence, has been successfully employed to generate the results presented below for the low-lying ionization energies of the hydrogen fluoride molecule as well as analogous ion-molecule energy differences for other interesting species, e.g.,  $N_2$ ,  $OH^-$ , and  $BeH^-$ . Let us now turn to an analysis of our results on the low-lying ionization potentials of HF.

### III. RESULTS AND DISCUSSION

Our calculations on the  $1\Sigma^+ \rightarrow 2\Pi$  and  $1\Sigma^+ \rightarrow 2\Sigma^+$  ionization energies of HF were carried out within both seventeen- and twenty-function Slater-type bases using a modification of Harris' DIATOM program to generate the necessary Hartree-Fock orbital energies and two-electron integrals. Tables I and II contain information describing the two basis sets and their respective (restricted) Hartree-Fock orbital energies and molecular orbital expansion coefficients, for occupied orbitals.

For the seventeen-function basis, the iterative solution of Eq. (4b) for vertical ( $R=1.7328$  a.u.) ionization to the  $2\Pi$  state of  $HF^+$  converged to an approximate ionization energy of 15.83 eV, which is to be compared to the Koopmans'-theorem prediction of 18.03 eV and the experimental photoionization result of Berkowitz *et al.*<sup>4</sup> of 16.01 eV. One minute and forty-three seconds of Univac 1108 computer time was required to calculate the Hartree-Fock orbital energies and the two-electron integrals in the Hartree-Fock basis; an additional one minute and two seconds was needed to compute the above ionization energy. The  $2\Sigma^+$  ionization potential generated by our method is 19.53 eV, which compares favorably with the experimental estimate<sup>12</sup> of 19.4 eV, and is a significant improvement over the Koopmans'-theorem prediction of 20.90 eV. Again, one minute and two seconds of time was required for this calculation.

Upon increasing the number of basis functions to twenty-

TABLE II. Twenty-function Hartree-Fock wavefunction for HF.  $R=1.7328$  a.u.,  $E=-100.0516$  a.u.,  $\epsilon_{1\sigma}=-26.3058$ ,  $\epsilon_{2\sigma}=-16.1251$ ,  $\epsilon_{3\sigma}=-0.7663$ ,  $\epsilon_{1\pi}=-0.6537$ .

$\sigma$ atomic orbitals	$1\sigma$	$2\sigma$	$3\sigma$	$\pi$ atomic orbitals	$1\pi$
F1s (7.9437)	0.9519	-0.2653	-0.0672	F2p (1.3584)	0.8783
F2s (1.9346)	-0.0004	0.4277	0.2392	F2p' (2.3291)	0.4579
F2p (1.4070)	-0.0009	-0.0120	0.2357	F2p'' (4.2614)	0.1323
F1s' (14.1095)	0.0859	0.0045	0.0024	H2p (1.7706)	0.0364
F2s' (3.2563)	0.0035	0.6001	0.1307		
F2p' (2.3732)	0.0021	-0.0741	0.3919		
F2p'' (4.2784)	-0.0024	-0.0241	0.2320		
F3s (9.9254)	-0.0407	-0.0283	0.0019		
H1s (1.3727)	-0.0002	-0.0084	-0.2556		
H1s' (2.4605)	0.0002	0.0705	-0.0338		
H2s (2.4615)	0.0002	0.0705	-0.0776		
H2p (2.9226)	0.0001	0.0192	-0.0281		

ty, the calculated ionization energy for the  $^2\Pi$  state changed to 15.87 eV, and the amount of computer time needed to carry out the Hartree-Fock calculation and the ionization potential calculation increased to six minutes and fifty seconds and one minute and fifty seconds, respectively. The ionization-energy calculation for the  $^2\Sigma^+$  state in the twenty-function basis required one minute and twenty-one seconds and resulted in an approximate energy difference of 19.49 eV. It is important to notice that the basis-set dependence of the time needed to compute these ion-molecule energy differences is dominated by the Hartree-Fock and two-electron integral transformation computation time.

Schaefer *et al.*<sup>13</sup> used a basis of similar size to compute potential curves for both  $^1\Sigma^+$  HF and  $^2\Pi$  HF\*. Using forty-three configurations for HF and one hundred and two configurations for HF\*, they obtained potential energy curves from which we estimate the vertical electronic ionization potential to be  $15.8 \pm 0.1$  eV which is in good agreement with our prediction. By forming  $H(\Delta E)$  using only the  $\beta=N$  terms in the first sum in Eq. (I-37), which generates our approximation to the ion-molecule Hartree-Fock energy difference, Eq. (4b) yields 15.60 eV for the lowest  $^2\Pi$  ionization energy. This prediction differs by 0.27 eV from our previous result of 15.87 eV, which contained the Hartree-Fock energy difference as well as the change in correlation energy which accompanies ionization. Schaefer's calculated adiabatic ionization potential in the Hartree-Fock approximation was 14.42 eV, whereas his configuration interaction result was 14.68 eV. The difference between these two numbers (0.26 eV), which indicates the contribution of electron correlation energy to the ionization potential, is very close to our vertical ionization energy difference of 0.27 eV. This implies that, for hydrogen fluoride, the ion-molecule correlation energy difference may not change appreciably for internuclear distances in the vicinity of the equilibrium bondlength of HF. Moreover, a comparison of the Koopmans' theorem ionization potential (18.03 eV) with the approximate Hartree-Fock prediction (15.60 eV) and the EOM result (15.87 eV) leads to the conclusion that charge redistribution effects are the most important corrections to Koopmans' theorem for this specific ionization potential. Correlation energy effects need be included only if one is interested in reaching an accuracy of  $\pm 0.3$  eV. In the light of these observations, it is important to point out that detachment energies of negative ions, whether computed as the electron affinity of the neutral or as the ionization potential of the ion, contain roughly equal contributions from charge redistribution and correlation energy change.

Based upon our experience in these calculations on HF and with similar calculation on other molecular systems,<sup>14</sup> we believe that a further increase in the size of our basis set would not alter the above ionization energies by more than  $\pm 0.05$  eV. Furthermore, we feel that, for calculations in which a sufficiently large atomic orbital basis has been employed, the limitations which are inherent to the approximations used in our approach give rise to a probable precision of  $\pm 0.15$  eV. As can

TABLE III. Summary of ionization potentials of hydrogen fluoride (in eV).

Ion state	Koopmans' theorem	$\Delta E_{HF}^a$	EOM <sup>b</sup>	Experiment <sup>c</sup>
$^2\Pi$	17.79	15.60	15.87	16.01
$^2\Sigma^+$	20.85	19.10	19.49	19.4

<sup>a</sup>Our approximate ion-molecule Hartree-Fock energy difference, which is computed by including only the  $\beta=N$  terms in the first sum of Eq. (I-37).

<sup>b</sup>The present third-order EOM results.

<sup>c</sup>Reference 4.

be seen from Table III, in which our results on HF are summarized, our calculated ionization potentials agree with the experimental measurements of Ref. 4 to within the estimated limits of our theory. The results of our calculations on  $N_2$  and  $OH^-$ , which will be reported elsewhere,<sup>14</sup> also indicate that our method is capable of yielding ion-molecule energy differences to within 0.15 eV. Although such uncertainties are much larger than the limits of reproducibility which are common to photoionization measurements ( $\pm 0.01$  eV), the difficulties associated with interpreting photoionization threshold data<sup>15</sup> makes the extraction of a vertical ion-molecule electronic energy difference from such data a procedure whose precision limits are often of the order of  $\pm 0.1$  eV. Thus, the results of our calculations on molecules and ions of chemical importance should be of much use and interest to experimentalists who are studying photoionization and photodetachment processes.

To supplement our research on ionization potential and electron affinity calculations, we are presently developing an efficient computer program which will permit us to compute the photoionization intensity corresponding to each ionization process, including shake up processes. In addition, we have available a program which carries out a direct calculation of the first-order reduced density matrix  $\gamma_{ij}$  of the parent species.<sup>16</sup> We believe that knowledge of this density matrix, which contains a great deal of information about the electron density and bonding in the parent, is very important to a more complete understanding of the chemical behavior and physical properties of the molecules and ions which we are studying.

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<sup>1</sup>J. Simons and W. D. Smith, *J. Chem. Phys.* **58**, 4899 (1973).

<sup>2</sup>J. Simons, *Chem. Phys. Lett.* **25**, 122 (1974).

<sup>3</sup>The lowest energy configuration of HF is  $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$ .

<sup>4</sup>J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, *J. Chem. Phys.* **54**, 5165 (1971).

<sup>5</sup>For good description of the properties of such Fermion creation and annihilation operators, see A. L. Fetter and J. D.

- Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
- <sup>6</sup>The molecular symmetry permits us to significantly reduce the complexity of our calculations. This simplification reduces the number of two-electron integrals which must be transformed to the Hartree-Fock basis.
- <sup>7</sup>If the parent molecule were open-shell, both single- and triple-excitations would also have to be included in  $|g\rangle$ .
- <sup>8</sup>T. Koopmans, *Physica* **1**, 104 (1934).
- <sup>9</sup>G. Purvis and Y. Öhrn have carried out second-order ionization potential calculations on  $N_2$  using propagator methods, which are very closely related to our EOM approach. In contrast to the present study, these workers did not include third-order terms in their self-energy, although they did investigate all of the ionization energies of  $N_2$ , including the shake up processes, as well as photoionization intensities. G. Purvis and Y. Öhrn, *J. Chem. Phys.* **60**, 4063 (1974).
- <sup>10</sup>In forming the product  $B_{i,naem} B_{j,naem}$ , only the second- and third-order terms are kept. A fourth-order contribution, which arises from the product of the second-order components of  $B_{i,naem}$  and  $B_{j,naem}$ , must not be included in the calculation.
- <sup>11</sup>See, for example, S. D. Conte, *Elementary Numerical Analysis* (McGraw-Hill, New York, 1965), p. 27.
- <sup>12</sup>This value was obtained from Fig. 12 of Ref. 4 in which the  $X^1\Sigma^+$  potential curve of HF and the  $^2\Pi$  and  $^2\Sigma^+$  curves of  $HF^+$  are shown. The ion curves were constructed by authors of Ref. 4 by employing Wahl's calculations of  $HF^+$  to determine the shape of the curve and adjusting both the minimum-energy point and the vertical displacement above the HF curve to fit the experimentally measured adiabatic ionization energy. Of course, the vibrational energies of HF and  $HF^+$  which enter into the experimentally determined value must be removed before making comparison with our vertical electronic results. Based on the potential curves shown in Ref. 4, we expect that our calculated ionization energies would not change by more than  $\pm 0.01$  eV if we had employed the Hartree-Fock bond length (1.70 a.u.) in our calculations rather than the experimental  $R_e$  (1.73 a.u.).
- <sup>13</sup>V. Bondybey, P. K. Pearson, and H. F. Schaefer III, *J. Chem. Phys.* **57**, 1123 (1972).
- <sup>14</sup>W. Smith, T. T. Chen, and J. Simons, "Theoretical Studies of Molecular Ions. Vertical Detachment Energy of  $OH^-$ ," *Chem. Phys. Lett.* (to be published); "Theoretical Studies of Molecular Ions. Vertical Ionization Potentials of the Nitrogen Molecule," *Chem. Phys. Lett.* (to be published).
- <sup>15</sup>For an excellent discussion of the techniques used to deconvolute experimental photoionization data, see P. M. Guyon and J. Berkowitz, *J. Chem. Phys.* **54**, 1814 (1971).
- <sup>16</sup>J. Simons, *J. Chem. Phys.* **59**, 2436 (1973).