Model for Proton Affinities and Inner-Shell Electron Binding Energies Based on the Hellmann–Feynman Theorem[1]

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Abstract: A potential energy model is developed for calculating proton affinities and relating them to inner-shell electron binding energies. The model is based on the Hellmann–Feynman theorem and employs CNDO/2 wave functions. A linear correlation is found between proton affinities and inner-shell binding energies within a homologous series of molecules. The proposed model is applied here to interpret the substituent effects, particularly those of alkyl groups, on proton affinities. The correlation between proton affinities and inner-shell binding energies can be interpreted in terms of a potential model because of similar relaxation effects upon addition of a proton or ionization of a core electron; *i.e.*, both processes can be described as the addition of a positive charge to a localized region of the molecule. The variation in binding energy of the nonbonding (highest occupied) orbital in aliphatic amines, alcohols, and ethers cannot be explained simply in terms of the relaxation potential model; ground state effects are of comparable magnitude here.

Calculations of proton affinities and binding energies of inner-shell electrons are closely related. In both cases one calculates an energy difference between species which differ primarily in the amount of charge they bear. One species may be considered to be derived from the other by the addition of a positive charge (or abstraction of a negative charge) to a particular nuclear center. The energy need for this must be strongly affected by the potential energy at the nuclear center. According to classical electrostatics, the change in energy with charge *is* the electrostatic potential. It is not surprising, then, that attempts have been made to interpret proton affinities and ESCA binding energies in terms of the electrostatic potential at a nucleus.[2] However, to our knowledge there has not yet appeared a quantitative model of proton affinities in terms of potentials. We present here such a model which, based on the Hellmann–Feynman theorem, gives a quantitative interpretation of chemical effects on proton affinities. Semiempirical (CNDO/2)[3] wave functions have been used to calculate the potentials rendering the model applicable to large molecules. The relationship between ESCA binding energies and proton affinities is derived and explicit correlations are presented.

Basic Formalism

Both ESCA chemical shifts and proton affinities will be interpreted in terms of energy differences between isoelectronic molecules whose Hamiltonians differ only in the amount of nuclear charge at one center. The energy of state n will be called E_n and will be assumed (Born–Oppenheimer approximation) to take the form

$$E_n = E_n^{\text{electronic}}(\{R_e\}_n) + E_n^{\text{vib}} + E_n^{\text{rot}} + E_n^{\text{trans}} \quad (1)$$

where $\{R_e\}_n$ represents the equilibrium nuclear coordinates for state n. We are interested in $E_{\text{ion}} - E_0$, where E_{ion} is the protonated or ionized state. For proton affinities it is assumed that $\Delta H_f = E_{\text{ion}} - E_0$. Note that proton affinity is defined as $-\Delta H_f$, or $E_0 -$

E_{ion}, and is therefore always a positive quantity. For both proton affinities and ESCA binding energies, it will be assumed that ΔE^{vib}, ΔE^{rot}, and ΔE^{trans} can be neglected and that $\{R_e\}_{\text{ion}}$ equals $\{R_e\}_0$. For small changes in geometry ($\Delta R < 0.1$ Å for a diatomic molecule), these assumptions can contribute errors amounting to several tenths of an electron volt, but they will cancel to some extent when calculating *relative* PA's and binding energies, especially for homologous molecules.

This model breaks down for proton affinities when there are large changes in geometry upon protonation. When there are nonbonding or "lone-pair" electrons in the nonprotonated state, the protonation site is well defined and $\Delta\{R_e\}$ is small. In this case the error in ΔE resulting from assumption of a fixed geometry is small because the values of $\partial E/\partial R$ at the chosen coordinates are zero or close to zero for both states. For nonprotonated states with symmetrical charge distributions (*i.e.*, no "lone pairs") such as methane,[4] $\Delta\{R_e\}$ may be large resulting in large errors in ΔE.

The model also fails for inner-shell binding energies when $\Delta\{R_e\}$ is large; under this condition ΔE^{vib} can be large due to sizable Franck–Condon factors for excited vibrational states of the ion.[5] The failure of this model to predict core-electron binding energies when the experimental spectrum consists of a number of unresolved vibrational bands has been discussed.[6] In this case the observed peak maximum corresponds to a "vertical" binding energy which contains a significant vibrational energy contribution.

E_{ion} will be approximated as $E(Z + 1)$, where the charge on a nucleus with a photohole or nuclear charge on the site of protonation has been increased by one over that of the initial state. Such an approximation has been found by Jolly[7] to give very good agreement with experimental inner-shell binding energies; it appears to introduce an error of only 5 to 10% in *relative* binding energies.

(1) Supported in part by the U.S. Army Research Office.
(2) (a) A. Pullman, *Chem. Phys. Lett.*, **20**, 29 (1973); C. Petrangolo and J. Tomasi, *ibid.*, **20**, 201 (1973); (b) D. W. Davis and D. A. Shirley, *ibid.*, **15**, 185 (1972), and references therein.
(3) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
(4) J. A. Pople, private communication.
(5) T. E. Sharp and H. M. Rosenstock, *J. Chem. Phys.*, **41**, 3453 (1964).
(6) R. E. Shaw and T. D. Thomas, *Chem. Phys. Lett.*, **22**, 127 (1973).
(7) W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970).
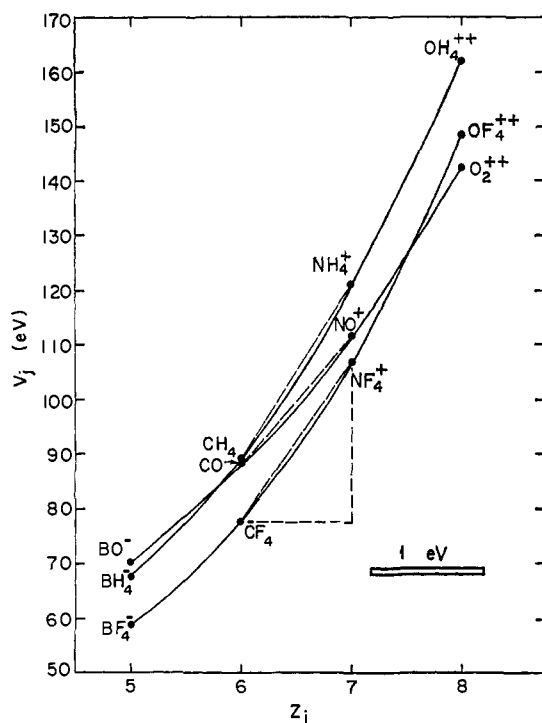
Figure 1. The potential energy of an electron at nucleus j, V_j, vs. the charge on nucleus j, Z_j, for three molecular systems. The linear relaxation energy for a C 1s transition in CF_4 is the area within the dotted line.

Instead of calculating $E(\{R_e\}_0, Z + 1) - E(\{R_e\}_0, Z)$ directly, it will be related to the electrostatic potential energy *via* the Hellmann–Feynman theorem. This theorem states that[8]

$$\frac{\partial E}{\partial \lambda} = \int \Psi^* \frac{\partial \mathcal{H}}{\partial \lambda} \Psi d\tau \qquad (2)$$

We are interested in the case where $\lambda = Z_j$, the charge on nucleus j. In this case

$$\frac{\partial \mathcal{H}}{\partial Z_j} = e^2 \sum_{k \neq i} \frac{Z_k}{R_{jk}} - e^2 \sum_i \frac{1}{r_{ij}} \qquad (3)$$

where R_{jk} is the distance between nuclei j and k and r_{ij} is the distance between electron i and nucleus j. The integral $\int \Psi^*(\partial\mathcal{H}/\partial Z_j)\Psi d\tau$ is the negative of the potential energy of an electron at nucleus j and will be called $-V_j(Z_j)$. V_j is a function of Z_j through the dependence of Ψ on Z_j. Equation 2 may be integrated to give

$$E(Z + 1) - E(Z) = -\int_Z^{Z+1} V_j(Z_j) dZ_j \qquad (4)$$

This integral will be approximated by a simple formula. V_j must be a monotonically increasing function of Z_j, for it can be shown that $\partial V_j/\partial Z_j \geq 0$ by the following argument. It is known[9] that the Hellmann–Feynman theorem may be differentiated to give the inequality

$$\frac{\partial^2 E}{\partial \lambda^2} \leq \int \Psi^* \frac{\partial^2 \mathcal{H}}{\partial \lambda^2} \Psi d\tau \qquad (5)$$

(8) H. Hellmann, "Einfuhrung in die Quantenchemie," Franz Deuticke and Co., Leipzig, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).
(9) B. M. Deb, *Chem. Phys. Lett.*, **17**, 78 (1972); J. N. Silverman and J. C. Van Leewen, *ibid.*, **7**, 37 (1970).

In the case of $\lambda = Z_j$, $\partial^2\mathcal{H}/\partial Z_j{}^2 = 0$ and

$$\frac{\partial^2 E}{\partial Z_j{}^2} = \frac{\partial(-V_j)}{\partial Z_j} \leq 0 \qquad (6)$$

Equation 6 precludes large oscillations of V_j with changes in Z_j. The generalized Hellmann–Feynman theorem as discussed above holds only for very restricted classes of wave functions, *i.e.*, exact, true Hartree–Fock, or other particularly optimized wave functions. Inspired by this theorem, we propose the following technique using approximate wave functions. We obtain an estimate of the integral in eq 4 by assuming V_j to be a linear function of Z which passes through its calculated values at Z and $Z + 1$. This is shown for several molecules in Figure 1. It appears that V_j does vary smoothly with Z_j; therefore, the integral may be reasonably approximated as

$$\int_Z^{Z+1} V_j(Z_j) dZ_j \cong \tfrac{1}{2}[V_j(Z + 1) + V_j(Z)] \qquad (7)$$

In a later section further comment will be made on the applicability of eq 7 when Z is zero. The integration of the Hellmann–Feynman theorem has been discussed previously and applied to some simple systems.[10]

CNDO/2 wave functions were used here to calculate $V_j(Z)$ and $V_j(Z + 1)$. Matrix elements were calculated exactly using formulas due to Roothaan,[11] but many two- and three-center matrix elements were set equal to zero in order to compensate for the zero-differential overlap approximation used in the determination of CNDO/2 wave functions. When V_j is calculated this way with CNDO wave functions, its value is generally close to that which would be calculated using *ab initio* wave functions and no approximations. The procedure is nearly identical with a point-charge potential model, where V_j is given by $Cq_j + \Sigma_{k \neq j} q_k/R_{jk}$. In fact, use of CNDO/2 values of the atomic charges, q_k, gives values of V_j which are close to those obtained by exact integration.[12] A detailed discussion of the procedure for calculating V_j with CNDO/2 wave functions has been presented;[13] it will not be repeated here.

Application to ESCA

This section will be restricted to general comments because the potential model has already been extensively applied to inner-shell binding energies.[2b,14] Equation 4 may be written as

$$E(Z + 1) - E(Z) \cong -\tfrac{1}{2}[V_j(Z + 1) + V_j(Z)] =$$
$$-V_j(Z) - \tfrac{1}{2}[V_j(Z + 1) - V_j(Z)] \qquad (8)$$

The last term on the right side of eq 8 is called the relaxation energy due to core-level photoemission. It reflects the movement of electrons toward the photohole. The relaxation energy for C 1s photoemission in CF_4 is represented in Figure 1 as the area of the triangle formed by the dotted lines, whereas $V_j(Z)$ is the area under the triangle between Z equal 6, Z equal 7,

(10) S. T. Epstein, A. C. Hurley, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, **47**, 1275 (1967).
(11) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).
(12) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **56**, 671 (1972).
(13) D. W. Davis and D. A. Shirley, *J. Electron. Spectrosc. Relat. Phenomena*, **3**, 137 (1974).
(14) U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **2**, 70 (1970).

and the base line. Obviously $V_j(Z)$ is the dominant term in eq 8. It appears that the error in eq 8, the area between the curved and dotted lines, is about 1 eV and may vary by at most a few tenths of an electron volt from molecule to molecule.

Much of the work on inner-shell binding energies implies that the relaxation term may be neglected when calculating relative binding energies.[14] In this case

$$\Delta E_B \cong \Delta[E(Z+1) - E(Z)] \cong -\Delta V_j(Z) \qquad (9)$$

The left side of eq 9 is called the equivalent-cores or thermochemical model of chemical shifts, while the right side is called the quantum-mechanical potential model. Both models have developed quite independently of each other; recently their relationship has been commented on.[15] The thermochemical model employs heats of formation [$\Delta H_f(Z+1)$ and $\Delta H_f(Z)$] to calculate core-level chemical shifts. Equations 8 and 9 imply that, conversely, relative heats of formation may be estimated from values of $V_j(Z)$ and $V_j(Z+1)$.

Hedin and Johansson[16a] have developed a model of *absolute* binding energies which is very similar in form to eq 8.[16b] In fact, their results were used to derive

$$\Delta E_B = -\frac{1}{2}[\Delta V_j(Z+1) + \Delta V_j(Z)] \qquad (10)$$

which has been used successfully to predict with CNDO wave functions core-level chemical shifts.[2b,17] Attempts at calculating inner-shell chemical shifts by taking the difference $E(Z+1) - E(Z)$ using energies from CNDO and MINDO wave functions[18] have resulted in poor agreement with experimental shifts; however, proper *ab initio* equivalent core calculations do give good shifts.[19]

Application to Proton Affinities

In order to use eq 8 to calculate proton affinities, it must be shown that the resulting error is negligible or constant. Obviously the error depends on the magnitude of the difference between the value of $\partial V_j/\partial Z_j$ at Z and the slope of the straight line between $V_j(Z)$ and $V_j(Z+1)$, which is $V_j(Z+1) - V_j(Z)$. Equation 8 implicitly assumes that this difference is small. Unlike inner-shell binding energies, one cannot easily interpolate in the case of proton affinities because $V_j(-1)$ is not known; $\Psi(-1)$ may not even be bound. Also, $\partial V_j/\partial Z_j$ cannot be easily estimated or even assumed to be large. If $\partial V_j/\partial Z_j$ were close to zero at Z_j equal to zero, and if V_j were a quadratic function of Z_j, eq 8 would overestimate the relaxation energy (which is dominant for the PA's of neutrals) by 50%. It is possible, however, to get some idea of the shape of

the curve of V_j vs. Z_j by calculating wave functions corresponding to nonintegral values of Z_j, for $0 \leq Z_j \leq 1$. In order to do this with CNDO wave functions, the necessary CNDO parameters were interpolated. The bonding parameter β_0 (which is roughly proportional to Z) was made proportional to Z_j, such that it assumed its usual value at Z_j equal to one. The diagonal elements of the Fock matrix were set proportional to Z_j^2 and the exponent of the 1s orbital centered around the proton was made a linear function of Z_j. With these interpolations, wave functions were calculated for nonintegral values of Z_j, and electrostatic potential energies. V_j approached their previously calculated values at Z_j equal to zero and one.

Potentials were calculated for Z_j equal to 0.25, 0.50, and 0.75. The error in eq 8 was estimated graphically as the area between the smooth curve drawn through the points from $Z_j = 0$ to $Z_j = 1$ and the straight line connecting $Z_j = 0$ and $Z_j = 1$.

The area (see Figure 1) was calculated for the transitions $NH^{2-} \rightarrow NH_2^-$, $NH_2^- \rightarrow NH_3$, $NH_3 \rightarrow NH_4^+$, $CH_3NH_2 \rightarrow CH_3NH_3^+$, $OH^- \rightarrow H_2O$, $H_2O \rightarrow H_3O^+$, $HF \rightarrow H_2F^+$, $CN^- \rightarrow HCN$, and $CO \rightarrow HCO^+$. It was found to be relatively independent of molecular structure; along the series NH^{2-} to CH_3NH_2, it gradually increased from 42 kcal/mol to 47 kcal/mol. It contributed about 1 kcal/mol to the calculated difference of 9 kcal/mol in the PA's of NH_3 and CH_3NH_2. The smallest value of this area was 38 kcal/mol for the transition $HF \rightarrow H_2F^+$, and the largest value was 47 kcal/mol for $CH_3NH_2 \rightarrow CH_3NH_3^+$. The average value of this area, as determined for the above species, was 43 kcal/mol. This average value was used in determining the calculated proton affinities by subtracting it from the numbers obtained in eq 8. These quantities are presented in Table I along with the calculated values of $V_j(0)$, $V_j(1)$, and the experimental proton affinities. The calculated and experimental PA's of

(15) D. A. Shirley, *Chem. Phys. Lett.*, **15**, 325 (1972).

(16) (a) L. Hedin and A. Johansson, *J. Phys. B*, **2**, 1336 (1969). (b) For *relative* binding energies their result reduces to $\Delta E_B \cong -\Delta[\frac{1}{2}(V' + V'^*)]$ where V' and V'^* are the respective potential energies of interaction (Coulomb plus exchange) of occupied and empty inner-shell orbitals with other orbitals. If one replaces ΔE_B by $\Delta[E(Z + 1) - E(Z)]$, V' by $V_j(Z)$, and V'^* by $V_j(Z + 1)$, one obtains eq 8. Thus, the Hedin-Johansson result suggests a relationship between the energy needed to add a positive charge to a system and the electrostatic potentials at the site of addition of the charge.

(17) M. S. Canna, D. W. Davis, and D. A. Shirley, *J. Chem. Phys.*, submitted for publication.

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(19) D. T. Clark and D. B. Adams, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1819 (1972).
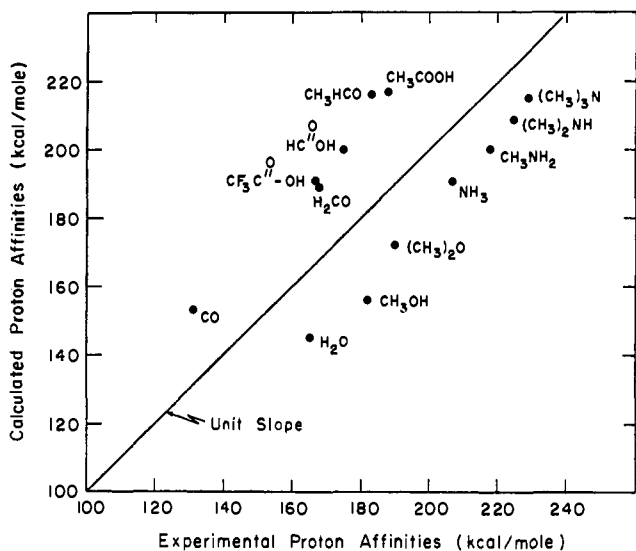
Table I

	$V_j(0)$, eV	$V_j(1)$, eV	$\frac{1}{2}[V_j(0) + V_j(1)]$ − (linear error), kcal/mol	Exptl PA, kcal/mol	Ref
NH^{2-}	26.47	47.54	808	~650	21
NH_2^-	13.60	31.70	478	~380	21
NH_3	2.41	17.97	191	207	23
CH_3NH_2	2.17	18.95	200	218.4	23
$(CH_3)NH$	1.98	19.90	209	224.9	23
$(CH_3)_3N$	1.80	20.63	215	229.1	23
CN^-	11.49	30.67	442	338	21
OH^-	14.94	30.09	475	~380	21
CH_3O^-	12.68	29.98	448	–	–
H_2O	1.63	14.73	145	165	30
CH_3OH	1.35	15.93	156	182	30
$(CH_3)_2O$	1.31	17.36	172	190	30
HF	1.84	11.22	108	108	21
				(*ab initio*)	
CH_3F	1.94	13.49	135	–	–
CO	0.69	16.38	153	131	21
H_2CO	2.45	17.68	189	168	30
CH_3HCO	2.99	19.48	216	183	30
$HCOOH$	2.81	18.31	200	175	30
CH_3COOH	3.10	19.44	217	188	30
CF_3COOH	2.11	18.19	191	167	30
$CH_3C \equiv C^-$	10.65	31.78	444	–	–
$HC \equiv C^-$	11.32	31.49	449	–	–

Figure 2. Calculated proton affinities *vs.* experimental proton affinities of neutral species.

neutral species are plotted against one another in Figure 2. The geometries used in the calculations were obtained from ref 20 and 21. This model tends to exaggerate the energy of protonation of carbonyl oxygen and underestimates it for alcohols, ethers, and amines. However, within each group *relative* proton affinities are predicted correctly.

In general the calculated and observed proton affinities decrease with total negative charge on the nonprotonated species. This is due mainly to a decrease in $V_j(0)$, as the relaxation energy, $1/2[V_j(1) - V_j(0)]$, is not strongly dependent on charge. Also, calculated proton affinities exceed experimental values more so for anions than for neutrals. This may be due to the small basis set used in the CNDO/2 calculations. A similar effect was observed by Czimadia, *et al.*,[21] with *ab initio* calculations.

Substituent Effects on Proton Affinities

A preliminary attempt was made to predict substituent effects on proton affinities of neutral species. First, the effect of substitution of a methyl group for hydrogen was examined for protonation of nitrogen, oxygen, and fluorine. In all cases methyl group substitution raised the calculated PA's, and reasonable agreement with experiment was obtained. The calculations indicate that most of the effect of substitution occurs in the protonated species; the methyl group delocalizes some of the positive charge and allows a higher electronic population at the proton. This results in an increase in the potential energy at the proton. The importance of charge delocalization in these cases has been mentioned by other workers.[22,23] The calculations also indicate that methyl group substitution for hydrogen *lowers* the potential energy at the site of

protonation in neutral species, but this effect is several times smaller than in the protonated species. This is not unreasonable; *ab initio* calculations predict that the electrostatic potential energy at the carbon atom decreases upon methyl substitution ($CH_4 \rightarrow CH_3CH_3$).[24]

Next, we have examined substituent effects in the carboxylic acids HCOOH, CH_3COOH, and CF_3COOH for which experimental PA's are available. Protonation was assumed to occur at the carbonyl oxygen. The relative effects of the H, CH_3, and CF_3 groups were correctly predicted by the potential model. The substitution of CF_3 for CH_3 effects the calculated PA primarily through the ground state, *i.e.*, $\Delta V_j(0)$. Final state effects, *i.e.*, $1/2[\Delta V_j(1) - \Delta V_j(0)]$, are substantial as well as $\Delta V_j(0)$ when CF_3 is substituted for H. The CNDO/2 results indicate that the CF_3 group delocalizes charge about as well as the CH_3 group, but its "group dipole" and inductive effect (both of which operate in *both* species) are much stronger than those of either CH_3 or H. The higher group dipole and inductive effect of CF_3 over those of H *oppose* the effect of its higher capacity for charge delocalization. This results in similar potential energies at the sites of protonation in CF_3-$COOH_2^+$ and $HCOOH_2^+$. The major difference between the CF_3 and CH_3 groups is the separation of charge in CF_3, a difference which shows up in the potential energies of both the neutral and protonated states.

Finally, the potential model of proton affinities was applied to several anions. It predicted most of the relative proton affinities correctly, but it reversed the order of the observed[25] PA's of $HC\equiv C^-$ and $CH_3C\equiv C^-$. Table I indicates that substitution of CH_3 for H in $HC\equiv C^-$ affects the potential energies at the site of protonation of the neutral species and anion to a similar degree but in opposite directions. It is likely that the stabilization of $HC\equiv C^-$ is exaggerated by CNDO/2.

Correlations between ESCA Chemical Shifts and Proton Affinities

Prior to this work, it was pointed out that a correlation should exist between the basicities of alcohols and their oxygen 1s binding energies[26] because of the similar rearrangement of electrons (relaxation) which occurs upon addition of a proton or ionization of an inner-shell electron. The preceding sections of this paper also suggest such a correlation. Both processes are obviously well described as the addition of a positive charge to the same vicinity of the molecule, and both may be interpreted in terms of potential energies. Furthermore, it is expected that chemical effects on the corresponding potential energies will be somewhat related due to the proximity of the nuclear centers and the bonding of the proton to only the atom which is ionized.

Correlations between experimental PA's and inner-shell binding energies have been found here and by other workers[27] for amines and some oxygenated compounds. These are shown in Figure 3. The binding

(20) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

(21) A. C. Hopkinson, N. K. Holbrook, K. Yates, and I. G. Czimadia, *J. Chem. Phys.*, **49**, 3596 (1968).

(22) J. I. Brauman, J. M. Riveras, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(23) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94** 4726 (1972).

(24) L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties: Tabulated from SCF Calculations in a Gaussian Basis Set," Wiley-Interscience, New York, N. Y., 1972.

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(26) Richard Martin, Department of Chemistry, University of California, Berkeley, private communication.

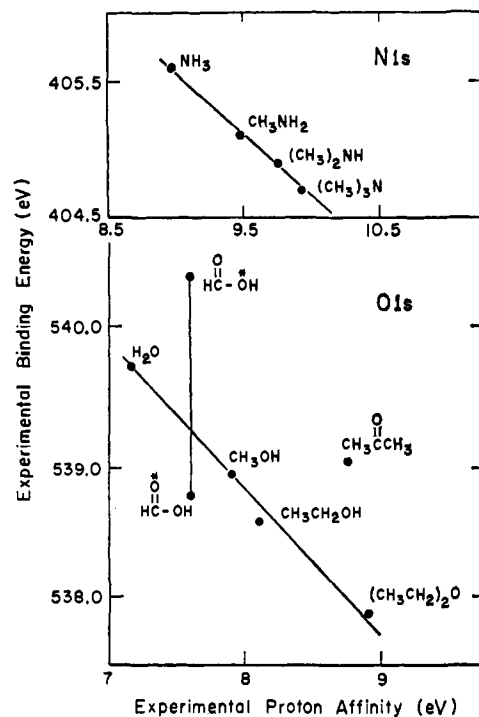(27) R. Martin and D. A. Shirley, *J. Amer. Chem. Soc.*, submitted for publication.

Figure 3. Experimental 1s binding energies vs. experimental proton affinities. Two points are plotted for formic acid, corresponding to the two oxygen 1s binding energies measured for formic acid. The site of protonation for formic acid is not known.

Figure 4. Calculated 1s chemical shifts vs. calculated proton affinities. The reference compounds are NH₃ and H₂O. The correlations for amines and for *all* oxygen compounds have a slope of about unity.

energies were obtained from ref 27, 28, and 29 and the proton affinities were obtained from ref 23 and 30. The correlation for the amines and the oxygenated compounds with only singly bonded oxygen is linear, with a slope very close to −1. According to the potential model presented here, the slope s of such a correlation is given by the following equation

$$ s = \frac{\Delta V_k^P(0) + \Delta V_k^P(1)}{\Delta V_j^e(Z) + \Delta V_j^e(Z + 1)} = \frac{\Delta V_k^P(0) + \Delta R_k^P}{\Delta V_j^e(Z) + \Delta R_j^e} \quad (11) $$

where $V_k^P(Z)$ and $V_j^e(Z)$ are potential energies at the site of protonation and at the core-ionized nucleus, respectively, and R is the relaxation energy $\frac{1}{2}[V(Z + 1) − V(Z)]$. The CNDO/2 calculations indicate that ΔR is the dominant term in eq 11 in both the numerator and denominator. It also assumes the same values for the PA's and 1s binding energies; hence the slope of 1 (the minus sign occurs because the experimental PA's are defined here as $E_{ground} − E_{ion}$ and vice versa for the binding energies). The calculations indicate further that changes in ΔR for these compounds are due primarily to differences in the ability of substituents to absorb and delocalize positive charge as discussed in the preceding section.

In the case of the oxygen compounds, however, two (formic acid and acetone) do not fall on the correlation. The potential model indicates that several factors may contribute to such a lack of correlation.

(1) Changes in ground-state potential energies due to substituent changes tend to be larger at the atom to be

ionized than at the site of protonation. This occurs because, within the formalism of molecular orbital theory, there is *no* atomic contribution to the ground-state potential energy at the site of protonation. Changes in this potential energy must come from extraatomic contributions.

(2) Large changes in the bonding (hybridization) of the atom to be protonated tend to affect proton affinities more than inner-shell binding energies. The inner-shell binding energy is sensitive primarily to the total electron population at the host atom rather than the spatial orientation of these electrons. For example, CNDO/2 calculations predict that in passing from H₂O to H₂CO the electron population at oxygen decreases by about 0.1 unit of charge. This causes a decrease in the potential energy at the oxygen nucleus of ∼2 eV. However, the ground-state potential energy at the site of protonation *increases* from H₂O to H₂CO. This is no artifact of the choice of protonation site; in both the ground and protonated states of H₂O, the potential energy at the site of protonation is less than would be expected from a spherical distribution of oxygen valence electrons.

(3) Relaxation energies associated with inner-shell binding energies tend to be affected by substituent changes more so than relaxation energies associated with protonation. According to CNDO/2 estimates, the electron population at an atom generally increases more than the population at the site of protonation when the respective nuclear charges are increased by one. However, this effect is predicted to be considerably smaller than the first two.

The CNDO/2 calculations indicate that for acetone the first and second factors (ground-state effects) are more important than the third factor (relaxation). Were relaxation effects dominant, the point for acetone would fall below the correlation, rather than above. The calculations are not sufficiently accurate to determine the relative importance of the first two factors.

Theoretical binding energy shifts vs. theoretical proton affinities, both calculated from eq 8 using CNDO/2 wave functions, are presented in Figure 4. The calculations correctly predict the observed correlation for the amines but not for H₂O and CH₃OH. This is due to inaccuracy in the calculated oxygen 1s chemical shift.

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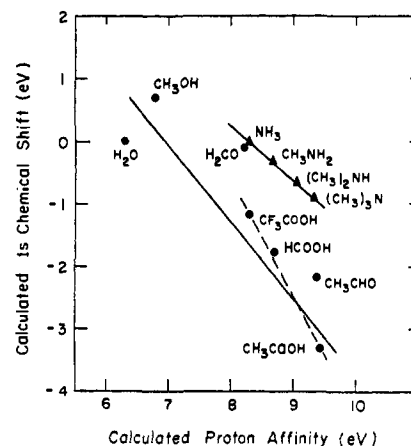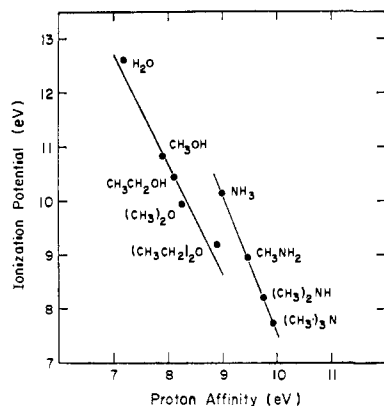(30) J. Lang and B. Munson, *J. Amer. Chem. Soc.*, 95, 2427 (1973).

Figure 5. The first ionization potential of aliphatic amines, alcohols, and ethers, *i.e.*, the nonbonding orbital, *vs.* experimental proton affinities.

Table II

	First IP, eV	Ref	PA, eV	Ref	CNDO/2 orbital energies, eV
H₂O	12.61	a	7.16	e	17.83
CH₃OH	10.83	b	7.89	e	15.50
CH₃CH₂OH	10.46	b	8.11	e	–
(CH₃)₂O	9.94	b	8.24	e	14.51
(CH₃CH₂)₂O	9.20	c	8.89	e	–
NH₃	10.17	d	8.98	f	16.27
CH₃NH₂	8.96	c	9.47	f	14.42
(CH₃)₂NH	8.21	c	9.75	f	13.55
(CH₃)₃N	7.75	c	9.93	f	13.09

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The correlation for the carboxylic acids has a slope greater than 1; this is attributed to the first factor mentioned above.

Finally, we have observed that the first ionization potential of aliphatic amines, alcohols, and ethers, *i.e.*, the nonbonding orbitals, correlates linearly with proton affinity and 1s binding energy. In Figure 5 is plotted the first ionization potential (adiabatic) *vs.* the proton affinity and Table II gives values of the ionization potentials. The correlation has a slope greater than 2. The preceding sections of this paper suggest that the variation in these binding energies will be due primarily to the variation in potential energy associated with relaxation if the nonbonding orbital remains highly localized about a single atom in both the ground state and final state. CNDO/2 wave functions indicate that the non-bonding orbital is delocalized in both the ground and ionic state and that much of the variation is due to ground-state effects. In H₂O and NH₃ the nonbonding orbital is composed primarily of 2p and 2s oxygen and nitrogen AO character, respectively. In both the alcohols and amines, the nonbonding orbital loses 2s character and becomes more delocalized upon substitution of alkyl groups for hydrogen. Consequently, the orbital energy decreases, providing a sizable contribu-

tion to the decrease in binding energy. However, the variation in PA's (and 1s binding energies) for these molecules is due almost entirely to relaxation (final state effects). Thus, we conclude that the linear correlations of Figure 5, if not fortuitous, cannot be explained on the basis of our simple potential model.

Conclusions

A model for predicting relative proton affinities and inner-shell binding energies has been proposed. The model, which uses CNDO/2 wave functions and is based on the Hellmann–Feynman theorem, provides an interpretation of substituent effects on proton affinities and binding energies. In particular, alkyl substitution raises the proton affinities of neutrals through delocalization of positive charge. There exists a linear correlation between proton affinities and binding energies within a series of homologous molecules. This correlation, or lack of it, can be rationalized within the formalism of the potential model.