Prediction of Proton Affinities and Protonation Sites using a Multivariate Linear Correlation

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We have shown, for a large set of compounds, including oxygen, nitrogen, and carbon bases, that it is possible to express the gas-phase proton affinities (PA) as a linear function of 1*s* binding energies *and* first ionization potentials. This multivariate correlation holds for molecules of different homologous series and we conclude that it contains the two most important factors which contribute to the basicity of a given molecule. We have also shown that some species which deviate from single correlations between PAs and 1*s* binding energies, *e.g.* *NN*-dialkylanilines, naphthalene, *etc.* fit our multivariate correlation very well. These systems are stronger bases than expected from the 1*s* ionization energy of their basic centres, due to their special ability to accommodate a highly localized positive charge. We have shown that similar correlations can be obtained using orbital energies, calculated using an STO-3G minimal basis set, instead of experimental ionization energies. Several cases are fully discussed.

IN the last few years considerable effort has been devoted to the study of the intrinsic basicity of organic molecules,[1] since high-pressure spectroscopy,[2,3] ion cyclotron resonance spectroscopy,[4] and even measurements of relative rates of protonation of two bases permit[5] the determination of relative proton affinities (PA), in the gas phase, with high accuracy. In fact, at present, the gas-phase PAs of >300 compounds are known. Moreover, these gas-phase experiments have been of great help in explaining the fundamental concept of basicity and those effects which influence this property. Often, gas-phase basicities follow the opposite trends to those observed in solution, and nowadays it is possible to measure solvation effects quantitatively, since PAs, both in the gas phase and in solution, can be determined. As a consequence, one can isolate those effects which affect the intrinsic basicity of a molecule from those which arise from the interaction between base and solvent.

Almost simultaneously with this development, Martin and Shirley[6] and Davis and Rabalais[7] established the existence of a linear relationship between gas-phase PAs and 1*s* binding energies, based on the formal similarity between the addition of a proton to a neutral molecule and the removal of a core electron from the same molecule. Such a relationship has been proved to hold for a variety of oxygen, nitrogen, phosphorus, and sulphur compounds.[6-11]

Recently, Brown and Tse[12] have shown that such a correlation breaks down when the site of protonation and ionization are not the same or when protonation causes substantial geometry changes.

It has also been proved that, for homologous series of compounds, there exists a linear correlation between the first ionization potential and the gas-phase PA.[10,13,14] However, Staley *et al.*[15] have shown, from studying this kind of correlations for nitriles, that caution must be exercised in choosing the correct ionization potential, especially when dealing with molecules possesing equivalent lone pairs leading to resonance stabilization of the cation.

These correlations have been useful in two ways: to predict intrinsic PAs from inner-shell ionization energies[8,16,17] (or first ionization potentials[10]) and to assign correctly bands in the photoelectron spectrum of a given compound, from its gas-phase PA.[15]

Different theoretical approaches[18-21] have been developed to help in the interpretation of experimental results. All of them are concerned with the calculation of the PA (which can be directly compared with the experimental value, since solvation effects are absent) and the prediction of the preferred protonation site. From the experimental point of view, the most basic position of a molecule could only be determined in very few specific cases, by means of sequential deuterium exchange reactions.[22] It must be noted that the correlation between experimental 1*s* binding energies and gas-phase PAs is not always useful for this purpose,[9] since it is not easy to measure, with enough accuracy, the 1*s* binding energies of all centres which can possibly undergo protonation in a molecule. Therefore, these predictions are usually obtained from theoretical calculations.

The correlation between 1*s* orbital energies, obtained from an SCF calculation, and experimental gas-phase PAs has been successfully used in predicting protonation sites.[21,23] These correlations are valid provided the relaxation energy involved in the removal of a core-electron[6] is practically the same for all compounds in a series, as in anilines,[21] pyridines,[24] aromatic compounds which protonate on the ring,[21] *etc.*

Nevertheless, some bases deviate significantly from the correlation between gas-phase PAs and 1*s* binding energies (or 1*s* orbital energies), which cannot be explained by the arguments of Brown and Tse.[12] Perhaps, one of the most striking cases is that of naphthalene, whose gas-phase PA is 11.0 kcal mol^{-1} higher than that of benzene.[25] Although no experimental value for the C_{1s} binding energy for this compound has been reported, the 1*s* orbital energy (at the STO-3G level) is almost identical[21] with that of benzene; therefore its PA should resemble that of benzene. This anomaly cannot be due to the fact that the site of ionization does not coincide with the site of protonation, since in naphthalene there is only one kind of basic site (carbon atoms) and it is unlikely that drastic geometrical changes take place upon protonation in naphthalene but not in benzene.

NN-Dimethylaniline and 1-aminonaphthalene pose, similarly, an interesting question as to whether they are nitrogen or ring bases.

Moreover, the correlation of PA and 1*s* binding energies can be applied only to homologous series of compounds.

The aim of this is to propose a new correlation based on a simultaneous linear relationship between the gas-phase PAs with 1*s* binding energies *and* the first ionization potentials. We shall show that such a correlation corresponds to a new analysis of the formal similarity between the protonation process and the creation of an electron-hole in the inner-shell of a neutral molecule and has the advantage of being more general than single correlations and is capable of providing an interpretation of the basicity of the specific cases mentioned above.

PA as a Function of 1*s Binding Energies and First Ionization Potentials*.—We shall present in this section the analysis of the linear dependence of gas-phase PAs on 1*s* binding energies *and* first ionization potentials. In this part we have used the experimental values of these magnitudes to avoid errors due to the use of Koopmans' theorem for the calculation of vertical ionization potentials. We shall come to this problem later.

The linear relationship between gas-phase PAs and core-binding energies was originally postulated by Martin and Shirley [6] and Davis and Rabalais,[7] in making a formal analogy between the core-level ionization reaction and the protonation process, and was first tested on series of oxygen-containing molecules.

According to Martin and Shirley [6] process (1) which defines the 1*s* binding energy is similar to (2) since in

$$\mathrm{(RR'R'')COH} \longrightarrow \mathrm{(RR'R'')C\overset{+}{O}H} + e^- \qquad \Delta H = E_\mathrm{B}(1s) \quad (1)$$

$$\mathrm{(RR'R'')COH} + \mathrm{H}^+ \longrightarrow \mathrm{(RR'R'')COH_2}^+ \qquad \Delta H = -\mathrm{PA} \quad (2)$$

both cases, the alcohol must accommodate the presence of a highly localized positive charge on or near the oxygen.

Although this argument is basically correct, it must be kept in mind, as pointed out by Brown and Tse,[12] that the first process is a vertical one, in the Frank–Condon sense and the second one may be considered as adiabatic, since the protonated species are fully relaxed, both geometrically and electronically. This implies that reaction (2) can be considered as a two step process: (a) the positive charge is localized on the oxygen atom [which can be taken as a reaction similar to (1)] and (b) the molecule undergoes a drastic reorganization of its charge distribution. Actually, in the final state, the initially bare proton has a non-negligible (usually >0.5e) electronic charge density. It is also clear that step (a) has a noticeably local character and it might be well described by a process, as for reaction (1), which, although affected in some manner by the molecular charge reorganization, also has a predominant local character. Step (b) has more of a molecular character, since the transfer of electronic charge from the base to the proton should depend on the ability of the molecule to donate electronic charge to the bare proton, and it might be adequately described by the first ionization potential of the molecule. This reasoning seem to be borne out by the fact that there is a good correlation between gas-phase PAs and the charge transferred to the proton during the protonation process.[26,27]

Moreover, it has been well established that the presence of alkyl groups at the basic site of the molecule yields a considerable increase of the base strength,[28,29] due to the ability of these groups to stabilize positive charge at that site, manifested by a higher polarizability and a lower ionization potential of the molecule.

It should be noticed that although there is a relaxation energy term accompanying variations of the 1*s* binding energies,[30] this term measures the energy of a relaxation process different from that which takes place upon protonation. In the core-ionization reaction, the relaxation occurs to fill an electron-hole in the inner-shell of a heavy atom (oxygen, in this particular case). In the protonation process, on the contrary, the electron-hole is placed in an *additional* centre (the proton) and the charge transfer depends more on the capacity of the molecule to donate charge, than on the particular site to which the proton is going to be attached.

We now discuss several families of compounds making use of the ideas presented in this section. The linear relationships between experimental gas-phase PAs, 1*s* binding energies, and the first IP are obtained by a least-squares technique.

(a) *Nitrogen bases*. We consider here primary, secondary, and tertiary amines and anilines. We include in each family those compounds for which the three quantities above are known with enough accuracy. They are listed in Table 1.

To analyse the influence of the two terms on the variations of the PA, all magnitudes are in eV relative to ammonia. The least-squares fitted correlations found were (3)—(5) for primary, secondary, and tertiary amines, respectively.

$$\Delta\mathrm{P}A = -\,0.493\,\Delta\mathrm{IE(N_{1s})} - 0.186\,\Delta\mathrm{IP} - 0.0003, \qquad \sigma_\mathrm{PA} = 0.003\ \mathrm{eV} \quad (3)$$

$$\Delta\mathrm{PA} = -\,0.449\,\Delta\mathrm{IE(N_{1s})} - 0.209\,\Delta\mathrm{IP} - 0.0002, \qquad \sigma_\mathrm{PA} = 0.01\ \mathrm{eV} \quad (4)$$

$$\Delta\mathrm{PA} = -\,0.419\,\Delta\mathrm{IE(N_{1s})} - 0.234\,\Delta\mathrm{IP} - 0.0001, \qquad \sigma_\mathrm{PA} = 0.001\ \mathrm{eV} \quad (5)$$

Several facts should be emphasized. (a) All these correlations show deviations which are much smaller than the deviations obtained using single correlations [PA *versus* IE($\mathrm{N_{1s}}$) or PA *versus* IP]. Figure 1 presents the experimental PAs *versus* the values calculated from

TABLE 1

1s Ionisation energies, vertical ionization potentials, and proton affinities, for nitrogen-containing molecules

	Compound	$IE(N_{1s})$/eV [a]	IP/eV [b]	PA/eV (kcal mol^{-1}) [b]
1	Ammonia	405.5	10.85	8.89 (205.0)
2	Methylamine	405.15	9.66	9.28 (214.1)
3	Ethylamine	404.96	9.42	9.41 (217.1)
4	n-Propylamine	404.88	9.35	9.47 (218.5)
5	n-Butylamine	404.86	9.32	9.49 (219.0)
6	Isopropylamine	404.80	9.32	9.51 (219.4)
7	s-Butylamine	404.72	9.30	9.56 (220.5)
8	t-Butylamine	404.67	9.25	9.60 (221.3)
9	Cyclohexylamine	404.72 [c]	9.12	9.60 (221.3)
10	*NN*-Dimethylamine	404.91	8.92	9.56 (220.5)
11	*NN*-Diethylamine	404.55	8.63	9.76 (225.1)
12	*NN*-Dipropylamine	404.45	8.54	9.86 (227.4)
13	*NN*-Dibutylamine	404.41	8.51	9.90 (228.4)
14	*NN*-Isopropylamine	404.29	8.40	9.93 (228.9)
15	Pyrrolidine	404.60 [c]	8.75	9.73 (224.3)
16	Piperidine	404.58 [c]	8.66	9.77 (225.4)
17	Trimethylamine	404.80	8.53	9.73 (224.3)
18	Triethylamine	404.36	8.03	10.02 (231.2)
19	Tripropylamine	404.20	7.92	10.12 (233.4)
20	1,4-Diazabicyclo-octane	404.67 [d]	7.52	9.98 (230.1)
21	Aniline	405.45 [d]	8.05 [e]	9.17 (211.5)
22	*p*-Methoxyaniline	405.29 [d]	7.82 [f]	9.32 (215.0)
23	*m*-Methylaniline	405.34 [d]	7.82 [g]	9.29 (214.3)
24	*p*-Methylaniline	405.33 [d]	7.81 [g]	9.29 (214.3)
25	*p*-Chloroaniline	405.58 [d]	8.25 [h]	9.09 (209.6)
26	*p*-Fluoroaniline	405.59 [d]	8.18 [g]	9.08 (209.4) [d]
27	*m*-Chloroaniline	405.66 [d]	8.26 [h]	9.04 (208.6)
28	*m*-Fluoroaniline	405.61 [d]	8.32 [g]	9.03 (208.1)
29	*N*-Methylaniline	405.22 [d]	7.75 [h]	9.46 (218.2)
30	*N*-Ethylaniline	405.01 [d]	7.56 [f]	9.62 (221.9)
31	*NN*-Dimethylaniline	405.11 [d]	7.37 [e]	9.70 (224.8)
32	*NN*-Diethylaniline	404.73 [d]	6.99 [i]	9.99 (230.4)
33	*N*-Ethyl-*N*-methylaniline	404.91 [d]	7.37 [f]	9.87 (227.7)
34	1-Aminonaphthalene	405.37 [d]	7.30 [j]	9.45 (217.9) [d]
35	*m*-Aminoaniline	405.30 [d]	7.60 [f]	9.69 (223.5) [d]

[a] The $IE(N_{1s})$ values are taken from ref. 8, and have been corrected to reproduce the values reported in ref. 34 for the series of methylamines, unless otherwise noted. [b] All values of vertical ionization potentials and gas-phase PAs correspond to measurements at 298 K, taken from ref. 33, unless otherwise noted. [c] Values taken from ref. 9. [d] Taken from ref. 12. [e] Taken from ref. 35. [f] Taken from ref. 36. [g] Taken from ref. 38. [h] Taken from ref. 37. [i] Taken from ref. 40. [j] Taken from ref. 39.

equations (3)—(5), respectively. (b) The results obtained confirm the mechanism presented above. As expected, the coefficient which measures the variation of the first IP increases from primary to tertiary amines, coinciding with the increasing polarizability in the three series.[41] This is ratified by studying the correlation in the series NH_3, $MeNH_2$, Me_2NH, Me_2N, in which the basicity, in the gas phase, increases in the same order as the polarizability ($NH_3 < MeNH_2 < Me_2NH < Me_3N$); therefore it is easy to conclude that the polarizability change is the one which most affects the basicity within this series. Our correlation shows such behaviour [equation (6)].

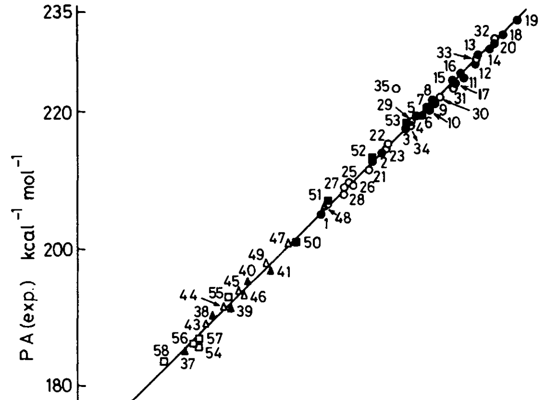

FIGURE 1 Experimental PAs of nitrogen, oxygen, and carbon bases *versus* calculated PAs obtained using a multivariate correlation in which the PA is expressed as a linear function of experimental 1*s* binding energies *and* first ionization potentials. For key see Tables 1 and 2

$$\Delta PA = -0.112\ \Delta IE(N_{1s}) - 0.324\ \Delta IP - 0.010 \quad (6)$$

Perhaps the most important feature is that it is possible to find a unique correlation (7) for all the aliphatic

$$\Delta PA = -0.410\ \Delta IE(N_{1s}) - 0.240\ \Delta IP - 0.024, \quad \sigma_{PA} = 0.01\ \text{eV} \quad (7)$$

amines with quite a small standard deviation. This means that the multivariate correlation we propose contains the most important features for adequately describing the protonation process. The standard deviation for this general correlation is a little worse than those corresponding to each homologous series. This probably indicates that some other factors, such as small geometrical distortions upon protonation, which will be different for primary, secondary, and tertiary amines, should also be included.

A slight drawback of multivariate correlations is that they cannot be easily visualized. Setting $a = b$ in equation (7) is equivalent to a linear correlation between ΔPA and the sum ΔIE(N_{1s}) + ΔIP. We present in Figure 2 such a correlation {which obeys the equation $\Delta PA = 0.293\ [\Delta IE(N_{1s}) + \Delta IP] - 0.031$, $\sigma_{PA} = 0.02$ eV}. This *approximate* expression correlates the three series (while single correlations hold only within homologous series of compounds) and this can be taken as an indication of the goodness of expression (7).

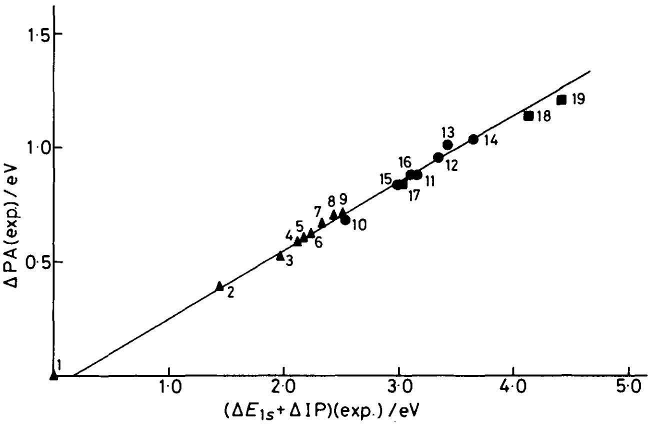

FIGURE 2 Experimental PAs relative to NH_3, for primary, secondary, and tertiary amines as a function of the sum [ΔIE(N_{1s}) + ΔIP]. For key see Table 1

For the following discussion it is more convenient to use absolute values since, in this way, the predicted PA can be directly obtained from the corresponding equations.

The correlation found for anilines obeys equation (8).

$$PA = -0.6548\ IE(N_{1s}) - 0.3235\ IP + 277.28,\ \sigma_{PA} = 0.009\ eV \quad (8)$$

It is remarkable that it is possible to define a unique correlation which holds for all primary amines and primary anilines, indicating again, that our multivariate correlation is more general than single correlations [equation (9)].

$$PA = -0.6857\ IE(N_{1s}) - 0.0893\ IP + 287.91,\ \sigma_{AP} = 0.012\ eV \quad (9)$$

Similar correlations (10) and (11) were found for the pairs secondary amines-*N*-alkylanilines and tertiary amines-*NN*-dialkylanilines.

$$PA = -0.5709\ IE(N_{1s}) - 0.0847\ IP + 241.47,\ \sigma_{PA} = 0.009\ eV \quad (10)$$

$$PA = -0.5280\ IE(N_{1s}) - 0.1557\ IP + 224.80,\ \sigma_{PA} = 0.013\ eV \quad (11)$$

Some results deserve more detailed discussion. Equation (8) gives a value for the PA of 1-aminonaphthalene of 217.8 kcal mol^{-1} which agrees quite well with the experimental value of 217.9 kcal mol^{-1}. This seems to indicate that this compound is a nitrogen base, although it has been suggested [23] that the ring PA is *ca.* 3 kcal mol^{-1} higher than nitrogen PA. This is a typical example in which the single correlation between PAs and 1*s* binding energies would fail. According to our model, 1-aminonaphthalene has a PA higher than that expected from its N_{1s} binding energy due to the high polarizability of the molecule and its low molecular ionization potential. Unfortunately this conclusion cannot be fully verified because no experimental value of the C_{1s} binding energies are known for this molecule and it is not possible to predict its ring proton affinity.

As had been shown by Brown and Tse,[12] *NN*-dimethylaniline, *NN*-diethylaniline, and *N*-ethyl-*N*-methylaniline have PAs which lie quite far from the linear correlation between experimental gas-phase PAs and 1*s* binding energies. Also, we have previously estimated [21] that ring protonation should be favoured by *ca.* 10 kcal mol^{-1} over nitrogen protonation, in the particular case of *NN*-dimethylaniline. However, equation (11) predicts for these three molecules, PA values (224.6, 230.6, and 227.1 kcal mol^{-1}, respectively) strikingly close to the experimental values (224.8, 230.4, and 227.7 kcal mol^{-1}, respectively), suggesting that they are nitrogen bases. We believe that, once more, these compounds do not fit the single correlation between PAs and N_{1s} binding energies, not only due to possible geometrical changes upon protonation, as recently suggested by Brown and Tse,[12] but mainly due to the fact that the presence of two alkyl substituents at the basic site increases the ability of the molecule to accommodate a positive charge (reflected by a low IP) favouring protonation at the nitrogen site.

This is not the case with *m*-aminoaniline which also deviates [12] from the linear correlation between PAs and N_{1s} binding energies, since this compound deviates also significantly (see Figure 1) from the multivariate correlation between PAs and N_{1s} *and* IP. This seems to confirm previous conclusions [42] which indicate that *m*-aminoaniline is protonated preferentially on the ring.

(b) *Oxygen bases.* We have studied similar correlations for three kinds of oxygen-containing molecules (listed in Table 2) which are bases: alcohols, aldehydes, and amides.

The least squares fitted correlations (12)—(14) were found for the alcohols, aldehydes, and amides, respectively.

$$PA = -0.3509\ IE(O_{1s}) - 0.2090\ IP + 199.52,\ \sigma_{PA} = 0.015\ eV \quad (12)$$

$$PA = -0.2345\ IE(O_{1s}) - 0.4620\ IP + 139.20,\ \sigma_{PA} = 0.015\ eV \quad (13)$$

$$PA = -0.2952\ IE(O_{1s}) - 0.2808\ IP + 170.36,\ \sigma_{PA} = 0.008\ eV \quad (14)$$

These equations are consistent with the mechanism presented in this paper. (i) In the alcohols, the substituent is directly bound to the basic centre (the oxygen atom); in consequence, the nature of the substituent

TABLE 2

1*s* Ionization energies, vertical ionization potentials, and proton affinities, for oxygen-containing molecules

Compound	IE(O_{1s}) [a]/eV	IP [a]/eV	IE(N_{1s}) [e]/eV	PA [b]/eV (kcal mol^{-1})
36 Water	539.65	12.61		7.50 (173.0)
37 Methanol	539.10	10.95		8.02 (184.9)
38 Ethanol	538.80	10.62	1	8.25 (190.3)
39 n-Propanol	538.55	10.49		8.30 (191.4)
40 t-Butyl alcohol	538.35	10.25		8.46 (195.0)
41 Phenol	538.90	8.73 [c]		8.54 (197.0)
42 Formaldehyde	539.42	10.88 [b]		7.69 (177.2)
43 Acetaldehyde	538.60	10.20 [b]		8.19 (188.9)
44 Propionaldehyde	538.60	9.99 [b]		8.30 (191.4)
45 n-Butyraldehyde	538.50	9.85		8.39 (193.6)
46 n-Pentaldedhyde	538.30	9.82		8.38 (193.3)
47 Benzaldehyde	537.75	9.54		8.71 (200.8) [d]
48 Acetophenone	537.15	9.35		8.92 (205.8) [d]
49 Acetone	537.90	9.71		8.55 (197.2)
50 Formamide	537.96 [e]	10.13 [f]	406.45	8.73 (201.4) [e]
51 *N*-Methylformamide	537.48 [e]	9.77 [f]	406.19	8.97 (206.8) [e]
52 *NN*-Dimethylformamide	537.09 [e]	9.14 [f]	405.96	9.24 (213.1) [e]
53 *NN*-Dimethylacetamide	536.78 [e]	8.81	405.63	9.46 (218.2) [e]

[a] Values taken from ref. 10, unless otherwise noted. [b] Taken from ref. 33. [c] Taken from ref. 43. [d] Taken from ref. 44. [e] Taken from ref. 12. [f] Taken from ref. 37.

affects not only the polarizability of the molecule (reflected in the IP term) but also, and to a higher degree, the electrostatic potential at the oxygen [reflected in the IE(O_{1s}) term, see refs. 31 and 32]. (ii) In the aldehydes the substituents are not directly bound to the oxygen atom, and therefore, little variation should be expected on the electrostatic potential at this centre; the main change on the polarizability of the molecule is a consequence of the increasing ability of the substituents (H, CH_3, C_2H_5, *etc.*) to stabilize the positive charge and thus the IP term dominates. (iii) Amides constitute a particular case of the previous series, since the NH_2 substituent produces remarkable inductive effects, with a greater influence on the electrostatic potential at the basic centre than alkyl substituents, resulting in a larger participation of the IE(O_{1s}) term.

Phenol is an exception among the alcohols and was not included in equation (12), since until now it has not been possible to definitely prove whether it is an oxygen or a ring base.[45] Using equation (12) we have obtained a PA of 197.7 kcal mol^{-1} quite close to the experimental value of 197.0 kcal mol^{-1}, which would indicate that phenol is an oxygen base. We shall come later to this particular problem.

We have used equation (12) to predict the PAs of the three alcohols listed in Table 3, for which the O_{1s} ionization energy and the IP are known, but whose gas-phase PA has not been measured. The values obtained are consistently higher (from 1—3 kcal mol^{-1}) than those predicted by Benoit and Harrison [10] using a single correlation between PAs and 1*s* binding energies. However, their single correlation underestimates [10] the PA values for n-propyl alcohol and t-butyl alcohol, while our multivariate correlation yields the correct values (see Figure 1).

TABLE 3

1*s* Ionization energies, vertical ionization potentials, and predicted PA for three aliphatic alcohols

Compound	IE(O_{1s})/ eV [a]	IP/eV [a]	PA/eV (kcal mol^{-1}) [b]
Isopropyl alcohol	538.4	10.44	8.39 (193.5)
n-Butyl alcohol	538.65	10.43	8.30 (191.5)
s-Butyl alcohol	538.60	10.23	8.36 (192.9)

[a] Values taken from ref. 10. [b] Values calculated using equation 12.

For carbonyl compounds it is interesting to note that equation (13) holds for aliphatic aldehydes and for benzaldehyde. No ketones were included to obtain this equation, because, to our knowledge, the three magnitudes included in the correlation are known only for two molecules, acetone and acetophenone; equation (13) predicts, in both cases, PAs (197.8 and 205.7 kcal mol^{-1}, respectively) in quite good agreement with experimental values (197.2 and 205.8 kcal mol^{-1}, respectively).

In obtaining equation (14) for amides we included formamide, whose PA has been recently reported by Taft and cited in ref. 12. This confirms the fact that the PA of this compound is *ca.* 3.6 kcal mol^{-1} lower than that of ammonia, rather than 5.4 kcal mol^{-1} as inferred from the single correlation of PA with IE(O_{1s}).[12]

2-Pyridone constitutes another interesting system for several reasons: (a) this compound appears to deviate from the linear correlation between PAs and IE(O_{1s}), for amides, although it has been suggested [12] that its basicity must be quite similar to that of pyridine (PA = 220.4 kcal mol^{-1}); (b) there is a tautomeric equilibrium between 2-pyridone and 2-hydroxypyridine which has received much attention; [46-48] (c) from this equilibrium it has been possible to establish that the PAs of 2-hydroxypyridine and 2-pyridone cannot differ by more than 0.58 kcal mol^{-1}.[47]

Using equation (14) and the experimental values of the O_{1s} ionization energy (536.66 eV) [48] and the IP (8.62 eV) [49] for 2-pyridone, we have obtained an oxygen PA for this compound of 219.8 kcal mol^{-1}, which lies only 0.6 kcal mol^{-1} below that of pyridine. This confirms that these two compounds should have similar basicity, but the most important point is that, once more, an exception to a single correlation rule obeys a multivariate correlation.

To investigate point (c) we have obtained a similar correlation for several pyridines,* which permits us to estimate the nitrogen PA of 1-hydroxypyridine [IE(N_{1s}) = 404.96 eV,[48] IP = 9.11 eV [49]]. The value obtained (220.3 kcal mol^{-1}) is 0.5 kcal mol^{-1} higher than the one obtained for 2-pyridone and in good agreement with the thermodynamical data for tautomeric equilibrium.[47]

We have also evaluated the intrinsic nitrogen PA of formamide, *N*-methylformamide, *NN*-dimethylformamide, and *NN*-dimethylacetamide, using equations (3)—(5), and the experimental values of the N_{1s} binding energies given in Table 2. The values obtained are 197.8, 203.1, 209.8, and 214.8 kcal mol^{-1}, respectively. Comparing these with the experimental values presented in Table 2 we see that, for amides, oxygen protonation is only slightly favoured over nitrogen protonation. It would be possible for these compounds in solution, to protonate on either basic site through a tautomerism with a changeover from *O*- to *N*-protonated species, depending on the interactions of base and solvent. This has been proposed, for benzamide, both on experimental [50] and theoretical [51] grounds.

(c) *Ring bases.* Finally we studied a series of aromatic compounds, listed in Table 4, which are protonated on the aromatic ring. The correlation found follows equation (15).

TABLE 4

1*s* Ionization energies, vertical ionization potentials, and PAs for aromatic compounds which protonate on the ring

Compound	IE(C_{1s})/ eV [a]	IP/eV	PA/eV (kcal mol^{-1}) [f]
54 Benzene	290.3	9.25 [b]	8.06 (185.8)
55 Toluene	290.1	8.80 [b]	8.37 (193.0)
56 Fluorobenzene	290.4	9.30 [b]	8.06 (186.0)
57 Chlorobenzene	290.8	9.07 [c]	8.06 (185.9
58 1,3,5-Trifluorobenzene	290.86	9.64 [d]	797 (183.8)
41 Phenol	290.20	8.73 [e]	8.54 (197.0)

[a] Values taken from ref. 43. [b] Taken from ref. 51. [c] Taken from ref. 37. [d] Taken from ref. 52. [e] Taken from ref. 35. [f] Taken from ref. 33.

$$PA = -0.1630\ IE(C_{1s}) - 0.3224\ IP + 58.45,\ \sigma_{PA} = 0.051\ eV \qquad (15)$$

For phenol, both the O_{1s} and the C_{1s} ionization energy (290.2 eV) [43] values are available. Therefore we can use equation (15) to predict the ring PA of this compound. The value obtained (191.6 kcal mol^{-1}) is considerably lower than the one obtained for oxygen protonation (which, as indicated before, agrees well with the experimental value). This would indicate that phenol is an oxygen base and not a ring base; however, this result must be treated with caution, since the σ_{PA} for this correlation is considerably greater than the ones obtained for the other families of compounds included in our study. This is probably due to the fact that the experimental assignment of the binding energy of each carbon atom, in an aromatic compound, is affected by a large error.[43] In these compounds the splitting of C_{1s} levels is not large enough to give well resolved peaks, and the photoelectron spectrum must be decomposed to its constituent bands by the spectrum simulation technique. The errors introduced in this way can be significant enough to cause variation of several kcal mol^{-1} in the predicted PA.

Another interesting case is that of naphthalene. Unfortunately, we could not find in the literature any experimental value for the C_{1s} binding energies of this compound, in the gas phase, and only the IP of 8.15 eV is available.[37] We have, therefore, estimated the C_{1s} ionization energy from the corresponding 1*s* orbital energy, obtained from an *ab initio* calculation at the STO-3G level.[21] To do that we have assumed that, within a homologous series, there is a linear correlation between experimental 1*s* binding-energies and 1*s* orbital energies. To obtain such a correlation we have included all compounds listed in Table 4, using experimental geometries. From this correlation we have estimated a C_{1s} binding energy for naphthalene of 290.28 eV, which substituted in equation (15) would give an estimated PA of 195.7 kcal mol^{-1}, 9.9 kcal mol^{-1} higher than that of benzene, and in very good agreement with the experimental value (11.1 kcal mol^{-1}).[25]

Again, naphthalene is a system which does not fit a linear correlation between PAs and 1*s* ionization energies, because the (estimated) C_{1s} binding energy indicates that it should be as basic as benzene; [21] however, naphthalene has a much lower IP than that of benzene and, according to our model, this feature is responsible for its high basicity.

Prediction of PAs from 1s *Orbital Energies and HOMO Energies.*—One important aim of our work is to show that experimental gas-phase PAs can be correlated with 1*s* orbital energies *and* the energy of the highest occupied molecular orbital (HOMO) which can be taken as measuring 1*s* binding energies and molecular ionization potentials, respectively. This implies the use of Koopmans' theorem, whose most important shortcoming is that it makes no allowance for relaxation of the electronic distribution after ionization (this is usually known as the frozen orbital approximation).

However, in previous publications [20-24] we have found, for homologous series, that the relaxation energy was practically constant when using 1*s* orbital energies. In a similar way one could admit that such an approximation will hold when using HOMO energies instead of IPs. Nevertheless, other factors, mainly correlation effects, can affect, in an uncertain sense, these relationships.[54] However, it seems clear that these correlation effects have little influence on core orbitals, where relaxation effects are more important.[54]

To test the validity of using HOMO and 1*s* orbital energies instead of experimental IPs and 1*s* binding energies, respectively, we have calculated new equations

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* The correlation obtained using twelve pyridine derivatives, obeys the equation: PA = 13.439 IE(N_{1s}) − 1.704 IP − 5 678.12 kcal mol^{-1}.

for molecules which contain either NH_2 or CHO groups, and whose PAs have been experimentally determined.

The HOMO and 1*s* orbital energies were obtained with a STO-3G minimal basis set using experimental geometries. The least-squares fitted correlation obtained for amines, whose orbital energies are presented in Table 5, is (16), practically parallel to that obtained using experimental ionization energies.

$$\mathrm{PA} = 1.1264\,E_{\mathrm{N}_{1s}} + 0.2633E_{\mathrm{HOMO}} + 480.46,\ \sigma_{\mathrm{PA}} = 0.009\ \mathrm{eV} \quad (16)$$

TABLE 5

1*s* Orbital energies, HOMO energies, and PAs for amines

Compound	$-E_{\mathrm{N}_{1s}}$/eV	$-E_{\mathrm{HOMO}}$/eV	PA (exp.)	PA (calc,)
			eV (kcal mol^{-1})	
Ammonia	416.42	9.567	8.889 (205.0)	8.890 (205.02)
Methylamine	416.30	8.539	9.284 (214.1)	9.297 (214.39)
Ethylamine	416.21	8.446	9.414 (217.1)	9.421 (217.26)
n-Propylamine	416.18	8.379	9.475 (218.5)	9.465 (218.28)
Isopropylamine	416.15	8.446	9.514 (219.4)	9.483 (218.70)
n-Butylamine	416.17	8.351	9.496 (219.0)	9.494 (218.92)
Isobutylamine	416.18	8.237	9.518 (219.5)	9.510 (219.32)
t-Butylamine	416.09	8.280	9.596 (221.3)	9.600 (221.39)
s-Butylamine	416.09	8.302	9.562 (220.5)	9.588 (221.10)
NN-Dimethylamine	416.50	7.785	9.562 (220.5)	9.547 (220.17) [a]
Trimethylamine	416.71	7.366	9.726 (224.3)	9.733 (224.45) [a]

[a] Values obtained using equation (17).

TABLE 6

1*s* Orbital energies, HOMO energies, and proton affinities for ethylene derivatives

Compound	$-E_{\mathrm{O}_{1s}}$/eV	$-E_{\mathrm{HOMO}}$/eV	PA (exp.)	PA (calc.)
			eV (kcal mol^{-1})	
Formaldehyde	552.75	9.619	7.684 (177.2)	7.693 (177.41)
Acetaldehyde	551.99	9.178	8.191 (188.9)	8.183 (188.70)
Propionaldehyde	551.91	9.023	8.300 (191.4)	8.300 (191.40)
n-Butyraldehyde	551.90	8.917	8.395 (193.6)	8.367 (192.96)
n-Pentaldehyde	551.89	8.898	8.382 (193.3)	8.377 (193.19)
Isopentaldehyde	551.84	8.892	8.382 (193.3)	8.394 (193.58)
Acetone	551.59	8.721	8.551 (197.2)	8.572 (197.68)

Correlation (17) with calculated orbital energies, within the series NH_3, $MeNH_2$, Me_2NH, Me_3N relative to NH_3

$$\Delta\mathrm{PA} = -\,0.158\,\Delta E_{\mathrm{N}_{1s}} + 0.363\,\Delta E_{\mathrm{HOMO}} - 0.002,\ \sigma_{\mathrm{PA}} = 0.005\ \mathrm{eV} \quad (17)$$

shows also parallel behaviour to that exhibited by equation (6), in the sense that the dominant term is that corresponding to the HOMO energy (IP) and the ratio $\Delta E_{\mathrm{N}_{1s}}/\Delta E_{\mathrm{HOMO}}$ is similar to the corresponding one in equation (6).

Correlation (18) found for the aldehyde series, whose orbital energies are presented in Table 6 is again quite

$$\mathrm{PA} = 0.3060\,E_{\mathrm{O}_{1s}} + 0.5833\,E_{\mathrm{HOMO}} + 182.44,\ \sigma_{\mathrm{PA}} = 0.009\ \mathrm{eV} \quad (18)$$

similar to the one obtained using experimental values [equation (13)].

We take the agreement between the equations found when using experimental ionization energies and calculated orbital energies for these two cases, as an indication that calculated data can be used to correlate proton affinities.

We tested this assumption on the nitrile family, for which experimental values of both IP and N_{1s} binding energies are available only for three compounds. We used nine compounds, listed in Table 7, to obtain equation (19) with a reasonably small standard deviation.

$$\mathrm{PA} = 0.5109\,E_{\mathrm{N}1s} + 0.0502\,E_{\mathrm{HOMO}} + 222.27,\ \sigma_{\mathrm{PA}} = 0.023\ \mathrm{eV} \quad (19)$$

Two facts must be emphasized: (a) the series includes aliphatic nitriles and species such as vinyl nitrile and benzonitrile; (b) the HOMO for all compounds listed in Table 7 is a π-molecular orbital. This last point is quite surprising, since very recently, Staley *et al.*[15] have found a good linear correlation between PAs and the nitrogen lone pair σ ionization potentials for this kind of compound, but no correlation with the CN-π ionization potential.

To investigate this apparent contradiction we have tried to correlate PAs using the energy of the nitrogen-pair orbital (NLPO) instead of the HOMO energy. The equation found is (20) which indicates that the multivariate correlation holds for both kind of ionization potentials.

$$\mathrm{PA} = 0.4333\,E_{\mathrm{N}_{1s}} + 0.1237\,E_{\mathrm{NLPO}} + 190.87,\ \sigma_{\mathrm{PA}} = 0.029\ \mathrm{eV} \quad (20)$$

We believe that, actually, there is no contradiction between the results of Staley *et al.*[15] and ours. It is easy to realize from Figure 3 in ref. 15 that there is also a linear relationship between PAs and the CN-π ionization potentials, with only three clear exceptions, ClCN, BrCN, and $CH_2(CN)_2$. The explanation is quite simple (and it is confirmed by our theoretical calculations):

ClCN and BrCN deviate from the linear correlation (of slope *ca.* 1.29 in Figure 3 of ref. 15 because in these two compounds the interaction between the halogen lone-pair and the π-orbitals of the CN group is very strong. Therefore, in these particular compounds one cannot speak of a CN-π ionization potential, since the π orbital involved in the ionization process is, by no means, a characteristic orbital of the CN group. This reasoning is confirmed by the fact that $ClCH_2CN$ does not deviate from the correlation, since the halogen atom is far enough from the CN group so that there is no strong interaction between them, and in this case, the π orbital which undergoes ionization is, indeed, an orbital localized on the CN group. The deviation shown by $CH_2(CN)_2$ has been adequately discussed by the same authors.[15] However, it should be pointed out that our multivariate correlation significantly improves the agreement between experimental and calculated values. This is probably so because the 1*s* orbital energies would be much less affected by the resonance stabilization mechanism proposed by Staley *et al.*[15] than first ionization potentials.

TABLE 7

1*s* Orbital energies, HOMO energies, nitrogen lone pair orbital (NLPO) energies, and PAs for nitriles

Compound	$-E_{N_{1s}}$/eV	$-E_{HOMO}$/eV	$-E_{NLPO}$/eV	PA [a]	PA [b]	PA [c]
				eV (kcal mol^{-1})		
HCN	418.64	12.027	13.423	7.76 (178.9)	7.784 (179.5)	7.818 (180.3)
MeCN	417.66	10.988	12.710	8.28 (190.9)	8.330 (192.1)	8.326 (192.0)
EtCN	417.59	10.838	12.536	8.36 (192.8)	8.378 (193.2)	8.378 (193.2)
Pr^{n}CN	417.53	10.775	12.383	8.40 (193.8)	8.408 (193.9)	8.425 (194.3)
Pr^{i}CN	417.46	10.683	12.318	8.50 (196.1)	8.456 (195.0)	8.469 (195.3)
Bu^{n}CN	417.46	10.571	12.005	8.49 (195.8)	8.460 (195.1)	8.503 (196.1)
CH_2=CHCN	417.85	9.034	12.783	8.32 (191.8)	8.334 (192.2)	8.235 (189 9)
$CH_2(CN)_2$	418.66	11.382	13.450	7.85 (181.0)	7.805 (180.0)	7.805 (180.0)
C_6H_5CN	417.60	7.973	12.307	8.53 (196.8) [d]	8.512 (196.3)	8.404 (193.8)

[a] Experimental values taken from ref. 33, unless otherwise noted. [b] Values calculated using equation (19). [c] Values calculated using equation (20). [d] Values taken from ref. 44.

Ethylene Derivatives.—We have included in our study those ethylene derivatives (see Table 8) for which the gas-phase PA is known, in an attempt to analyse the basicity of ambident reagents, which can present two typical basic sites, one of which is the $-CH_2$ group, *e.g.* keten, vinylamine, vinyl nitrile, *etc.*

The correlation obtained is (21). When applying this

$$PA = 1.4218\ E_{C_{1s}} + 0.4614\ E_{HOMO} + 437.51,\ \sigma_{PA} = 0.008\ eV \quad (21)$$

equation (21) to keten, one must choose among five gas-phase PAs reported in the literature, ranging from 196.8 ± 2 to 201.7 ± 1.2 kcal mol.[55-59] We have evaluated, using the corresponding 1*s* orbital energies (see Table 8) and equation (18) and (21), the intrinsic oxygen and carbon PAs, respectively. The values obtained were 194.3 kcal mol^{-1} for oxygen protonation and 201.1 kcal mol^{-1} for carbon protonation. This clearly agrees with the established fact that keten is not an oxygen base. Our calculated value is in better agreement with the experimental values reported by Vogt *et al.*,[56] Davidson *et al.*,[57] and Lias,[59] than with the one measured by Debrou *et al.*[55] (196.8 kcal mol^{-1}).

Vinyl nitrile was also studied with the nitriles. Here we evaluate its carbon PA using equation (21) and the corresponding C_{1s} orbital energy. The value obtained is considerably lower (117.8 kcal mol^{-1}) than the experimental one, which confirms that the basic site is on the nitrogen atom.

TABLE 8

1*s* Orbital energies, HOMO energies, and proton affinities for ethylene derivatives

Compound	$-E_{C_{1s}}$/eV	$-E_{O_{1s}}$/eV	$-E_{N_{1s}}$/eV	$-E_{HOMO}$/eV	PA [a]	PA [b]
					eV (kcal mol^{-1})	
CH_2=CH_2	299.86			8.835	7.09 (163.5)	7.098 (163.7)
MeCH=CH_2	299.43			8.256	8.02 (184.9)	7.790 (183.7)
Me_2C=CH_2	299.13			7.913	8.54 (196.9)	8.550 (197.1)
Me_2C=CHMe	299.29			7.404	8.56 (197.3)	8.563 (197.3)
CH_2CO	299.19	554.65		7.363	8.53—8.75 (196.8—201.7)	8.720 (201.1)
CH_2=$CHNH_2$	299.00		417.37	7.167		
CH_2=CHCN	301.19		417.85	9.034		

[a] Experimental values taken from ref. 33, except for CH_2CO (see text). [b] Values calculated using equation (21).

Finally, we studied vinylamine. As the experimental structure for this compound is not available we have adopted the following geometrical parameters: a C–C bond length (equal to that of acrolein) of 1.341 Å, a C–N bond length (equal to that of methylamine) of 1.474 Å, all CH bond lengths were set equal to 1.08 Å and NH bond lengths equal to 1.01 Å; the CCN angle was taken equal to 121°. Using the corresponding calculated orbital energies (see Table 8) and equations (16) and (21), respectively, we have estimated that carbon protonation is favoured over nitrogen protonation by 14.7 kcal mol^{-1}. This is not too far from the value obtained (18.7 kcal

mol^{-1}) in theoretical calculations using a DZ + D basis set.[60]

Conclusions.—We have shown, for a wide set of compounds, including oxygen, nitrogen, and ring bases, that there is a linear relationship between gas-phase PAs, 1*s* binding energies (BEs), and molecular ionization potentials. Since this multivariate correlation holds for molecules of different homologous series, one can conclude that it contains the two most important factors which contribute to the basicity of a given molecule. The weight of these two factors is always consistent with a mechanism which assumes that in the protonation process one can distinguish two steps, one of local character (localization of a positive charge on the basic site) quantitatively measured by the core binding energy of the basic centre and the other (transfer of electronic charge from the base to the bare proton) quantitatively measured by the molecular ionization potential.

We have also shown that some species which deviate significantly from the single correlation of PA with 1*s* BE, such as *NN*-dialkylanilines, naphthalene, *etc.*, fit our multivariate correlation very well. We conclude that those systems are stronger bases than expected from the 1*s* binding energy of their basic centres, due to their high polarizability, which facilitates considerably the accommodation of a highly localized positive charge.

The predicted PAs for 2-pyridone and 2-hydroxypyridine are in good agreement with data obtained from the thermodynamical study of the corresponding tautomeric equilibrium between these two species.

We have also shown that similar correlations can be obtained using orbital energies instead of experimental ionization energies. For nitriles, our correlations using theoretical values, indicate that there should exist a correlation using either the energy of the nitrogen lone pair orbital or the energy of the HOMO, which is a CN-π orbital. We conclude that the deviations observed for ClCN and BrCN are a consequence of the strong interaction between the lone pair orbitals of the halogen atom and the π orbitals of the CN group. As a consequence, in these systems the HOMO is no longer a CN-π orbital.

It must be pointed out that we have found that the coefficients in each of the equations presented in this paper can vary appreciably as the number of compounds used to obtain it increases. However, these variations are such that the new equation correlates all systems with a standard deviation very close to the previous one.

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REFERENCES

[1] See, for example T. X. Carroll, S. R. Smith, and T. D. Thomas, *J. Am. Chem. Soc.*, 1975, **97**, 659; D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, 1976, **98**, 318; P. Kollman and S. Rothenberg, *ibid.*, 1977, **99**, 1333; J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *ibid.*, p. 5417; Y. K. Lau, P. P. S. Saluja, P. Kebarle, and R. W. Alder, *ibid.*, 1978, **100**, 7328; D. H. Aue, L. D. Betowski, W. R. Davidson, M. T. Bowers, P. Beak, and J. Lee, *ibid.*, 1979, **101**, 1361; R. S. Brown, A. Tse, and J. C. Vederas, *ibid.*, 1980, **102**, 1174; D. H. Aue, H. M. Webb, W. R. Davidson, M. Vidal, M. T. Bowers, H. Golwhite, L. E. Vertal, J. E. Douglas, P. A. Kollman, and G. L. Kenyton, *ibid.*, p. 5151; D. S. Bomse and J. L. Beauchamp, *J. Phys. Chem.*, 1981, **85**, 488.

[2] W. R. Briggs, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, 1975, **94**, 5128.

[3] R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, 1976, **98**, 7452.

[4] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, jun., *J. Am. Chem. Soc.*, 1971, **93**, 4314.

[5] S. A. Mcluckey, D. Cameron, and R. G. Cooks, *J. Am. Chem. Soc.*, 1981, **103**, 1313.

[6] R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, 1974, **96**, 5299.

[7] D. W. Davis and J. W. Rabalais, *J. Am. Chem. Soc.*, 1974, **96**, 5305.

[8] B. E. Mills, R. L. Martin, and D. A. Shirley, *J. Am. Chem. Soc.*, 1976, **98**, 2380.

[9] R. G. Cavell and D. A. Allison, *J. Am. Chem. Soc.*, 1977, **99**, 4201.

[10] F. M. Benoit and A. G. Harrison, *J. Am. Chem. Soc.*, 1977, **99**, 3980.

[11] A. J. Ashe, M. K. Bahl, K. D. Bomben, W. T. Chan, J. K. Gimzewski, P. G. Sitton, and T. D. Thomas, *J. Am. Chem. Soc.*, 1979, **101**, 1764.

[12] R. S. Brown and A. Tse, *J. Am. Chem. Soc.*, 1980, **102**, 5222.

[13] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, 1972, **94**, 4728; 1973, **95**, 2699; 1975, **97**, 4136.

[14] W. G. Henderson, D. H. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, 1972, **94**, 4729.

[15] R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1976, **98**, 2081.

[16] S. R. Smith and T. D. Thomas, *J. Am. Chem. Soc.*, 1978, **100**, 5459.

[17] R. S. Brown and A. Tse, *Can. J. Chem.*, 1980, **58**, 694.

[18] W. J. Hehre, R. T. McIver, jun., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1974, **96**, 7196.

[19] O. Chalvet, C. Decoret, and J. Royer, *Tetrahedron*, 1976, **32**, 2927.

[20] J. Catalán and M. Yáñez, *J. Chem. Soc., Perkin Trans. 2*, 1979, 741.

[21] J. Catalán and M. Yáñez, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1631.

[22] B. S. Freiser, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1975, **97**, 6893.

[23] J. Catalán and M. Yáñez, *Chem. Phys. Lett.*, 1979, **60**, 499.

[24] J. Catalán, O. Mó, P. Pérez, and M. Yáñez, *J. Am. Chem. Soc.*, 1979, **101**, 6520.

[25] Y. K. Lau, P. P. S. Saluja, P. Kebarle, and R. W. Alder, *J. Am. Chem. Soc.*, 1978, **100**, 7328.

[26] W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topson, and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 5821.

[27] J. E. Del Bene, *J. Am. Chem. Soc.*, 1978, **100**, 1673.

[28] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, jun., *J. Am. Chem. Soc.*, 1971, **93**, 4314.

[29] R. L. Woodin and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1978, **100**, 501.

[30] D. W. Davis and D. A. Shirley, *J. Am. Chem. Soc.*, 1976, **98**, 7898.

[31] H. Basch, *Chem. Phys. Lett.*, 1970, **5**, 337.

[32] M. E. Swartz, *Chem. Phys. Lett.*, 1970, **6**, 631.

[33] D. H. Aue and M. T. Bowers, 'Gas-phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1979, vol. 2 and references therein.

[34] P. Finn, R. K. Pearson, J. M. Hollander, and W. C. Jolly, *Inorg. Chem.*, 1971, **10**, 378.

[35] T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2563.

[36] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, and J. T. Field, 'Handbook of Chemistry and Physics,' CRC Press, Cleveland, 1980—1981, 61st edn.

[37] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley-Interscience, New York, 1970.

[38] M. H. Palmer, W. Moyes, M. Spiers, and J. N. A. Ridyard, *J. Mol. Struct.*, 1979, **53**, 235.

[39] J. B. Birks, ' Photophysics of Aromatic Molecules,' Wiley-Interscience, London, 1970, pp. 457—460.

[40] D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.*, 1972, **17**, 90.

[41] J. Applequist, J. R. Cook, and K. K. Fung, *J. Am. Chem. Soc.*, 1972, **94**, 2952.

[42] S. K. Pollack, J. L. Devlin, III, K. D. Summerhays, R. W. Taft, and R. W. Hehre, *J. Am. Chem. Soc.*, 1977, **99**, 4483; K. D. Summerhays, S. K. Pollack, R. W. Taft, and W. J. Hehre, *ibid.*, 1977, **99**, 4485.

[43] T. Otha, T. Fujikawa, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2017.

[44] B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1977, **99**, 3214.

[45] J. Catalán and M. Yáñez, *J. Am. Chem. Soc.*, 1979, **101**, 3490 and references therein.

[46] P. Beak, *Acc. Chem. Res.*, 1977, **10**, 186 and references therein.

[47] D. H. Aue, L. D. Betowski, W. R. Davidson, M. T. Bowers, P. Beak, and J. Lee, *J. Am. Chem. Soc.*, 1979, **101**, 1361.

[48] R. S. Brown, A. Tse, and J. C. Vederas, *J. Am. Chem. Soc.*, 1980, **102**, 1174.

[49] C. Guimon, G. Garrabe, and G. Pfister-Guilluozo, *Tetrahedron Lett.*, 1979, 2585.

[50] M. Liler, *J. Chem. Soc., Perkin Trans. 2*, 1974, 71.

[51] J. Catalán and M. Yáñez, *Tetrahedron*, 1980, **36**, 665.

[52] M. H. Palmer, W. Moyes, M. Spiers, and J. N. A. Ridyard, *J. Mol. Struct.*, 1978, **49**, 105.

[53] R. Gilbert, P. Sauvagean, and C. Sandorfy, *Chem. Phys. Lett.*, 1972, **17**, 465.

[54] For a complete discussion on this topic see M. E. Schwartz, ' Application of Electronic Structure Theory,' ed. H. F. Schaefer III, Modern Theoretical Chemistry, 1977, vol. 4, p. 357.

[55] G. B. Debrou, J. E. Fulford, E. G. Lewars, and R. E. March, *Int. J. Mass. Spectrom. Ion Phys.*, 1978, **26**, 345.

[56] J. Vogt, A. D. Willianson, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1978, **100**, 3478.

[57] P. Ausloos and S. G. Lias, *Chem. Phys. Lett.*, 1977, **51**, 53.

[58] W. R. Davidson, Y. K. Lau, and P. Kebarle, *Can. J. Chem.*, 1978, **56**, 1016.

[59] S. G. Lias, ' Thermochemistry of Gaseous Ions,' NATO Advanced Study Institute Series B, 1979, vol. 40, p. 223.

[60] M. R. Ellenberger, R. A. Eades, M. W. Thomsen, W. E. Farneth, and D. A. Dixon, *J. Am. Chem. Soc.*, 1979, **101**, 7151.