

Lawrence Berkeley National Laboratory

Recent Work

Title

INHIBITION OF THREE NUCLEOTIDE POLYMERASES BY RIFAMYCIN DERIVATIVES

Permalink

<https://escholarship.org/uc/item/5982390z>

Authors

Thompson, Frances M.

Tischler, Allan N.

Adams, Jesse

et al.

Publication Date

1973-08-01

Submitted to Journal of
American Chemical Society

RECEIVED
LAWRENCE
RADIATION LABORATORY

LBL-2341
Preprint *2*

JAN 25 1974

LIBRARY AND
DOCUMENTS SECTION

THE RELATION OF CORE-LEVEL BINDING ENERGY
SHIFTS TO PROTON AFFINITY AND LEWIS BASICITY

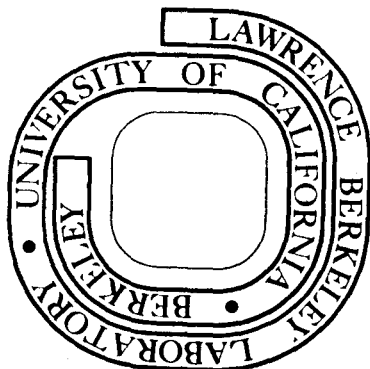
R. L. Martin and D. A. Shirley

December 1973

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545



LBL-2341
2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE RELATION OF CORE-LEVEL BINDING ENERGY SHIFTS TO PROTON
AFFINITY AND LEWIS BASICITY*

R. L. Martin and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

December 1973

Abstract

Gas-phase oxygen 1s binding energy shifts ΔE_B (O 1s) in simple aliphatic alcohols were found to decrease in the order:
water > methyl > ethyl > isopropyl > t-butyl. Comparison with potential-model calculations showed that the shifts are attributable to relaxation in the molecular-ion final state (polarization effects) rather than to the initial-state charge distribution (inductive effects). The ability of methyl groups to stabilize charge in the ion is consistent with the observation by Brauman and Blair that the gas-phase acidity order is t-butyl > ... > H₂O. The range of gas-phase acidities, which are not yet available, is expected to be comparable to that of ΔE_B (O 1s). It was predicted that ΔE_B (O 1s) $\sim -\Delta(\text{proton affinity})$ for these compounds. In fact the agreement between these two parameters is excellent: thus ΔE_B (O 1s) appears to measure relative Brønsted basicities: the ΔE_B (O 1s) vs $-\Delta(\text{PA})$ relation may be applicable to substituted alcohols (the CF₃CH₂OH point agrees very well with the above alcohols) and possibly to other functional groups. The N(1s) binding energy, which decreases in the order
NH₃ > CH₃NH₂ > (CH₃)₂NH > (CH₃)₃N, shows excellent agreement with $-\Delta(\text{PA})$ in these compounds. The calculated relaxation-energy (or polarization) contribution to

ΔE_B for both alcohols and amines agrees very well with the variation in the lone-pair ionization potential, thus giving quantitative support to a suggestion made by W. C. Price in 1947. The ΔE_B values for core electrons can be regarded as measuring Lewis basicity if the latter is extended to include nonbonding core orbitals. Thus I(3d_{5/2}) shifts in alkyl iodides are in excellent agreement with the O(1s) shifts in alcohols, with t-butyl iodide being a stronger Lewis base than methyl iodide. Core level shifts may be useful in predicting relative relativities at different sites in a molecule, because they depend on the proper combination of inductive and polarization shifts. Finally, the inverted acidity order of the aliphatic alcohols in solution may be understood in terms of extra-molecular polarization in the final state.

I. Introduction

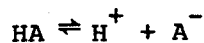
The relationship between molecular structure and reactivity is one of the central problems of chemistry. It may be divided into two parts. Qualitative questions about reactivity tend to focus on whether a reaction path exists that can take reactant R to product P. Principles such as orbital symmetry¹ can be applied to answer these questions. If a path exists for a given type of reaction, we may then be interested in its quantitative aspects; e.g., the extent to which the reaction proceeds. An important component of this second part is the relationship between the structures of the reactant and the product and the equilibrium constant for the rapid reversible reaction



In this paper we shall investigate the way in which a relatively new experimental parameter--the shift in core-level binding energy--can be related to certain reactions of the above type, particularly those involving gain or loss of hydrogen ions. In making the analogy between the core-level ionization reaction



and the ionization processes



or



we shall find it useful to generalize further the Lewis concept² of an acid as an electron acceptor and a base as an electron donor, to include core orbitals. By applying principles that have emerged from the theory of core-level shifts, we shall attempt to show how insight can be gained into the relative importance for acid-base reactions of inductive (initial-state) effects and polarization (final-state) effects.

Oxygen 1s binding energies of several simple alcohols were measured in the gas phase to test the ideas developed in this paper. These results are presented in Section II. They are compared with proton affinities in Section III. The Lewis basicity concept is extended to include core-level binding-energy shifts in Section IV. Acidities in solution are discussed briefly in Section V.

II. The O(1s) Shifts in Alcohols

Relative core-level binding energies of the oxygen 1s orbital were measured for isopropyl and t-butyl alcohols in the gas phase, using the Berkeley Iron-Free Spectrometer. These were combined with previously reported values for methanol³ and ethanol.⁴ The experimental techniques have been described earlier.⁵ This series was chosen to determine the effect that successive methyl substitution on the adjoining carbon would have on the O(1s) binding energy. An internal standard of water was used to enhance the accuracy of the measured shifts. The alcohol O(1s) shifts are given in Table I.

Table I. O(1s) binding energy shifts (eV).

Alcohol	Exptl. Shift	Predicted Shift ^d	
		GPM	RPM
H ₂ O	(0.0)	(0.0)	(0.0)
CH ₃ OH	-0.8 ^a	+0.38	-1.08
CH ₃ CH ₂ OH	-1.16(6) ^b	+0.20	-1.69
(CH ₃) ₂ CHOH	-1.24(1) ^c	-0.06	-2.26
(CH ₃) ₃ COH	-1.62(1) ^c	-0.16	-2.59
CF ₃ CH ₂ OH	-0.04(4) ^b		

^aReference 3.

^bReference 4.

^cThis work.

^dStandard bond lengths and bond angles with the nuclei in staggered rotational conformations were used for the CNDO/2 calculations. See J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory (McGraw-Hill Book Co., New York).

III. Comparison with Proton Affinities

In this section we discuss the relation between core-level binding energy shifts and acidity. The two subjects are first treated separately, with emphasis on the distinction between inductive and polarization effects.

In photoemission from the oxygen 1s orbital of an alcohol,



$$\Delta H = E_B(1s) , \quad (4)$$

the O(1s) binding energy $E_B(O\ 1s)$ is given by the difference between initial- and final-state energies,

$$E_B(O\ 1s) = E_f(RO^*H) - E_i(ROH) . \quad (5)$$

An approximate value of $E_B(O\ 1s)$ is given by (minus) the O(1s) orbital energy, $-\epsilon(O\ 1s)$, which may be obtained directly from a Hartree-Fock calculation on the ground state of ROH. In approximate discussions of core-level binding-energy shifts, it is common to approximate ΔE_B by $-\Delta\epsilon$.⁶ Now ϵ and E_B are related by

$$E_B^i = -\epsilon^i - E_R^i \quad (6a)$$

$$\Delta E_B^i = -\Delta\epsilon^i - \Delta E_R^i , \quad (6b)$$

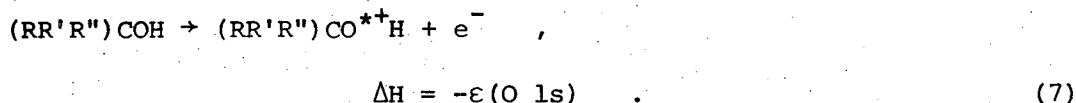
where E_R^i is the "relaxation energy" accompanying loss of an electron from core level i and Δ implies the comparison of a given core level (such as O(1s)) between two molecules. The use of $\Delta\epsilon$ for ΔE_B is equivalent to considering only the

differences between ground-state properties, i.e., inductive effects. This approach is quite useful when inductive effects are dominant. Thus the higher carbon 1s binding energy in CF_4 than in CH_4 is quite properly attributed to the withdrawal of electronic charge from carbon by the four fluorines, leaving a more positive environment at the carbon atom. Since the C(1s) orbital acts as a probe of the electrostatic potential near the carbon nucleus, the resultant binding-energy shift can be quite accurately calculated without resorting to ab initio SCF methods. Intermediate-level molecular-orbital models such as the CNDO method have been successfully applied to calculate these inductive shifts. For example, a version developed in our Laboratory--the Ground-State Potential Model (or GPM) approach--gives good predictions of core-level shifts for certain classes of molecules.⁷ However, the series of alcohols studied in this research does not comprise such a class, and the GPM predictions of O(1s) shifts, listed in Table I, fail badly to reproduce the experimental trend.

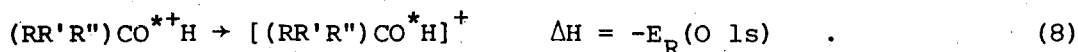
In considering only ground-state, or inductive, effects above we have neglected a crucial parameter of great chemical importance: the internal polarizability of the molecule. As an electron is removed from the O(1s) orbital in an alcohol, other electrons in the molecule are polarized toward the resultant positive hole. Since this polarization occurs adiabatically as part of the photoemission process, it is manifest as a reduction of the binding energy by an amount E_R , the "relaxation" energy. Thus ΔE_B^i in equation 6b will follow $\Delta \epsilon^i$ only to the extent that ΔE_R^i can be neglected. Now it happens that E_R has a tendency to increase with molecular size. This can perhaps be best understood if the molecule in its final state is regarded as the neutral molecule plus an electron

hole of charge $+e$.⁸ The electronic charge distribution of the molecule will relax to "screen" the hole charge. In effect the hole charge is almost totally screened locally by polarization of charge $\sim -e$ to the oxygen atom. The molecule's excess positive charge thus moves to the outside of the molecule to minimize the Coulombic repulsion. Larger molecules can therefore minimize this repulsion most effectively. Since this process is adiabatic, the polarization occurs without transitions and the final state still has a vacancy in the $O(1s)$ orbital. The dependence of E_R on molecular size implies that the alcohols studied here should show a substantial ΔE_R effect. From the above argument $E_R(O 1s)$ should increase from H_2O to t -butyl alcohol, thereby reducing $E_B(O 1s)$ monotonically from H_2O to t -butyl alcohol, in contrast to the GPM estimates in Table I. Relaxation effects can be taken into account by using another method based on CNDO orbitals, the Relaxation Potential Model (RPM) approach.⁹ RPM values of $\Delta E_B(O 1s)$, also given in Table I, show much better agreement with experiment than do the GPM estimates. In particular the trend is correctly predicted.

To express the above discussion in chemical terms, the $O(1s)$ photoemission process in equation 4 can be split into two hypothetical reactions. In the first an $O(1s)$ electron is removed but the orbitals do not relax and the alcohol goes to an imaginary unrelaxed intermediate state in which the oxygen atom has an additional charge of $+1$:



Shifts in the energy of this "reaction" are inductive shifts. In the second step the remaining electronic charge distribution relaxes to screen the positive hole, carrying the molecule into its actual final state,



Shifts in the energy of this "reaction" are polarization shifts. The two types of shifts are not separately observable because the unrelaxed intermediate state does not really exist. The "reactions" in equations 7 and 8 sum to the real process, in equation 4, for which the energy change $E_B = -\epsilon - E_R$ is observed. Finally, if the O(1s) binding energies between two alcohols ROH and R'OH could be compared at equilibrium,

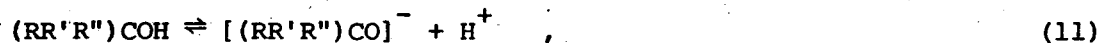


the heat of this reaction would be $\Delta H = \Delta E_B(\text{O } 1s)$. Neglecting entropy effects the equilibrium constant would be given by

$$K \cong e^{\Delta E_B/kT} \quad (10)$$

Turning now to the relative acidities of these alcohols, let us make an analysis analogous to that given above. Note that gas-phase acidities are of interest here. This distinction is important because the order of the relative acidities of these alcohols is reversed between aqueous solution and the gas phase, with H_2O being most acidic in the former and least in the latter.^{10,11} In relating gas-phase acidities to binding-energy shifts in the following discussion we shall employ ideas that may be useful for understanding the solvent-reversal effect, to which we shall return in Section V.

In the gas phase the acid dissociation equilibrium for an alcohol

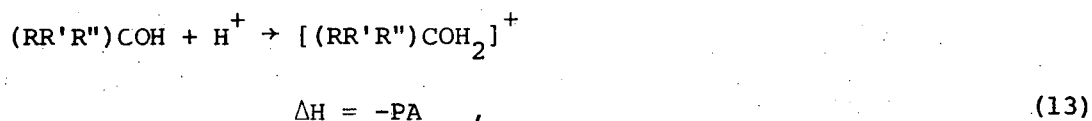


is influenced by both inductive and polarization effects. In the case of alcohols, variations in the inductive effect throughout a series of molecules would be expressed as a variation in the O - H bond strength. As Brauman and Blair have pointed out, however,¹¹ the O - H bond strength is essentially constant at 104 kcal/mole for all the simple alcohols: thus variations in their acidities arise mainly from variations in the electron affinities (EA) of the alkoxy radicals. This electron-affinity variation would in turn arise largely through differences in the alkoxy radicals' abilities to stabilize an additional negative charge. Since this "stabilization" process is very similar to equation 8, but for a negative charge, it seems reasonable to expect the variations in energy of these two "relaxation" processes to be closely related. We therefore predict the acid constants of two of these simple alcohols to be approximately given by

$$RT \ln \frac{K_1}{K_2} \cong \Delta EA \cong -\Delta E_R(O 1s) \approx \Delta E_B(O 1s) \quad , \quad (12)$$

where $\Delta EA = EA^{(2)} - EA^{(1)}$ and similarly for ΔE_R and ΔE_B . The $E_B(O 1s)$ in Table I would therefore predict a range of approximately 1.6 eV in the electron affinities of the respective alkoxy radicals. Unfortunately there are not enough electron-affinity data available to test this prediction at present.

Gas-phase proton-attachment reactions provide an even better quantity to compare with $\Delta E_R(O 1s)$ in simple alcohols--the proton affinity, PA. Thus the reaction



is very similar to equation 4. In both cases the alcohol must accommodate to the appearance of a highly-localized positive charge on or near the oxygen: an

electron hole in the 1s orbital in equation 4 or a proton in equation 13. The proton attachment reactions can also be broken up into two hypothetical steps. In the first, the analogue of equation 7, the proton would attach to the oxygen without flow of charge in the molecular framework:



Here the product is written to indicate that the excess positive charge is localized on the proton, and $E(H^+)$ would be a "rigid-molecule" proton dissociation energy. In the second hypothetical step the electronic charge in the alcohol relaxes to shield the added positive charge, and the excess charge is effectively distributed over the whole molecule. This step, the analogue of equation 8, can be written



where $E_R(PA)$ is a relaxation energy analogous to $E_R(O\ 1s)$ for the photoemission process. For a series of simple alcohols in which the charge on oxygen stays essentially constant from one member of the series to the next, the inductive term, $E(H^+)$ in equation 14, remains essentially constant. Variations in the proton affinity will then be given by

$$\Delta(PA) \cong \Delta E_R(PA) \quad . \quad (16)$$

For these same alcohols the variations in the O(1s) orbital energy should be small, for the same reasons. Thus from equation 6b,

$$\Delta E_B(O\ 1s) \cong -\Delta E_R(O\ 1s) \quad (17)$$

Now equations 8 and 15 are very similar to one another in their overall effect; namely, the relaxation of electronic charge to shield an excess positive charge on the oxygen. The incremental relaxation energies ΔE_R should therefore be nearly the same, and from equations 16 and 17 one would expect

$$\Delta(PA) \cong -\Delta E_B(O\ 1s) \quad (18)$$

That is, the variation in proton affinity of an alcohol should be nearly equal to the variation in the O(1s) binding energy. The negative sign in equation 18 is a consequence of the sign conventions for binding energy and proton affinity.

That equation 18 is rather accurately obeyed by the simple alcohols is illustrated in figure 1, in which the binding energy shifts for the simple alcohols from Table I are plotted against the proton affinities of these alcohols,¹²⁻¹⁴ listed in Table II. Also plotted is the CF_3CH_2OH point, to be discussed below. The good agreement between these two quantities provides a striking illustration of the close connection between core-level binding energy shifts and chemical properties. We note that this is not just an empirical correlation of unknown origin, but a straightforward consequence of a molecule's electronic charge distribution relaxing to shield an excess positive charge in two similar processes.

Before seeking to generalize the above result we must issue a caveat. The confirmation of equation 18 in figure 1 does not guarantee that the above argument is completely correct. In particular it does not imply that the

Table II. Proton affinities in simple alcohols (kcal).

Compound	PA
H ₂ O	165(2) ^a
CF ₃ CH ₂ OH	168(3) ^b
methanol	181(2) ^a
ethanol	186(2) ^a
isopropyl alcohol	193(3) ^a
t-butyl alcohol	198,206 ^a

^aThese proton affinities are adopted values, from references 12-14, with estimated error in last digit given parenthetically. Two values have been given for t-butyl alcohol: both are listed.

^bJ. L. Beauchamp, private communication.

quantities plotted are almost entirely variations in relaxation energies, as equations 16 and 17 would imply. In fact both the theoretical results in Table I and further evidence to be presented below imply that ΔPA and ΔE_B (0 1s) do in large measure arise from their ΔE_R terms. For this comparison of ΔPA with ΔE_B (0 1s), however, inductive (initial-state) effects would also make these two parameters tend to vary together. This is readily illustrated by re-writing equation 6b for this case and its proton-affinity analogue derived from equations 13 and 14:

$$\Delta E_B(0\ 1s) = -\Delta \epsilon(0\ 1s) - \Delta E_R(0\ 1s) \quad (6b')$$

$$-\Delta(PA) = -\Delta E(H^+) - \Delta E_R(PA) \quad (19)$$

If in going from one alcohol to another the oxygen becomes more negative, for example, then $\epsilon(1s)$, which is always negative for bound states, will increase, thereby decreasing $E_B(0\ 1s)$. The "rigid molecule" (inductive) contribution to the proton affinity, $E(H^+)$, will of course increase, as will PA, and $-\Delta(PA)$ will also be negative. Thus inductive effects as well as relaxation effects would shift $-\Delta PA$ and ΔE_B similarly, and equation 18 would still tend to hold.

From the above reasoning we can make, as a first step toward generalizing, the rather tentative suggestion that proton affinities and core-level binding-energy shifts may be comparable among a wider range of compounds than just the essentially non-polar simple alcohols. The comparison can be extended in two steps. First, a wider variety of functional groups could be considered. Thus methoxy, phenyl, or CF_3 groups could be attached to the α carbon, for example, and the resulting 0 1s binding-energy shifts could be compared with known

proton affinities, to test the prediction that $\Delta E_B(O\ 1s) \cong -\Delta(PA)$. Data on only one compound appear to be available for testing this prediction: the proton affinity and O 1s binding-energy shift in CF_3CH_2OH . When plotted on figure 1, the CF_3CH_2OH point shows excellent agreement with the trend for the simple aliphatic alcohols. We note that substitution of CF_3 for CH_3 in ethanol shifts both its PA and $E_B(O\ 1s)$ by about 1 eV. More data will be required before a definitive comparison can be made.

A second, larger extension would include other oxygen-containing functional groups in the comparison. Thus the proton affinities and O 1s binding-energy shifts in alcohols and acids could be compared, for example, to test the predicted $\Delta E_B(O\ 1s) \cong -\Delta(PA)$ relation. Unfortunately there are not enough O 1s binding energies and proton affinities available for the same molecules to test the validity of either of these extensions. It seems probable that the first prediction should hold, but the second is less likely to, because molecular geometries of different functional groups can change on proton attachment, while there is no geometry change on x-ray photoemission.

A somewhat different case is readily tested. This is the relation between the nitrogen 1s binding energy shifts, $\Delta E_B(N\ 1s)$,¹⁵ and the variation in proton affinities^{16,17} of the series NH_3 , CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$. Very good agreement between these two quantities is found, as indicated in figure 2. This agreement is particularly impressive because in this case methyl groups are substituted for hydrogens directly on the photoemitting nitrogen atom. The reason that the range of $\Delta E_B(N\ 1s)$ and $\Delta(PA)$ is only about one eV for these amines appears to be that the inductive and polarization effects oppose one another, with the trend determined by the dominant polarization effect. Thus $E_B(N\ 1s)$ is larger in NH_3 than in $(CH_3)_3N$ even though the methyl groups tend

more to withdraw electronic charge from N than do the hydrogens.⁴ We infer from this result and the agreement between $\Delta E_B(N\ 1s)$ and $-\Delta(PA)$ that the sign of the variation in the gas-phase proton affinity for these amines is attributable to final-state polarization effects.

Another outgrowth of the above analysis is a possible explanation of the variation of the first ionization potential within these series of alcohols and amines. The first ionization potential decreases with methyl substitution in each case, by 2.64 eV from H_2O to t-butyl alcohol¹⁸ and by 2.33 eV from NH_3 to $(CH_3)_3N$.¹⁶ Many attempts have been made over the years to explain these variations in terms of chemical properties, particularly inductive effects due to methyl substitution. However, W. C. Price suggested as early as 1947 that "charge-transfer effects" in the molecular ion could account for a relatively large stabilization in the ion and a consequent lowering of the first ionization potential accompanying alkyl substitution.¹⁹ Inasmuch as the first ionization potential can be associated with ionization of an electron from the nitrogen or oxygen lone-pair orbital in these compounds, we may identify the above "charge transfer effects" as flow of electronic charge toward the N or O atom during photoemission. The relative stabilization energy would therefore be given approximately by the relative relaxation energy, which has been calculated for the alcohol (Table I, using $\Delta E_R = \Delta E_B(GPM) - \Delta E_B(RPM)$ and the amines (Table III of reference 4, using $\Delta E_R = \Delta V_R$). The variation in ionization potential would then be given by

$$\Delta(IP) \cong -\Delta E_R \quad (20)$$

This relationship actually holds surprisingly well, as shown in figure 3, especially for the carbon-containing molecules in each group. This good agreement

appears to establish the polarization (or extra-atomic relaxation) effect as the main contributor to the variation in the first ionization potential in these alcohols and amines.

IV. An Extension of Lewis Basicity

G. N. Lewis generalized the concept of basicity by defining a base as a substance having a lone pair of electrons that could be used to complete the valence shell of another atom.² This freed discussions of basicity from the necessity of including any particular ion, such as H^+ . From the preceding discussion of proton affinities and electron binding energies, it is evident that, while the former measure the Brönsted basicity, the latter are closely related to the Lewis basicity. In fact we need only extend Lewis's definition of basicity to include core-level "lone pairs" as well as those in the valence shell in order to utilize core-level binding energy shifts as one operational measure of the Lewis basicity. We note that these shifts--and the basicity--are comprised of two parts: the initial-state inductive effects and the final-state polarization effects. In studying chemical reactivity we are interested in both effects, in the particular combination given by the binding-energy shifts, rather than just the initial-state charge distributions. This combination of effects would be expected to carry over from the Brönsted bases discussed in Section III to compounds exhibiting Lewis basicity as defined above. Two examples of cases for which this result appears to be established are discussed below.

Iodine $3d_{5/2}$ core-level shifts and 5p lone pair shifts in HI and various iodides were reported and compared earlier.²⁰ The shifts were interpreted at that time as arising from inductive effects. It seems probable, however, in light of the foregoing discussion, that final-state polarization is in fact the dominant factor in these $I(3d_{5/2})$ shifts. If this is the case, one would expect the $I(3d_{5/2})$ binding energies to decrease in the order $HI > \text{methyl} > \text{ethyl} > \text{isopropyl} > \text{t-butyl}$, and to vary as do the $O(1s)$ shifts in the corresponding alcohols. Figure 4 shows that these expectations are quite accurately borne out.

Another case in which final-state polarization appears to be important is that of substituted nitroxides. The average N(1s) binding energy is 410.4 eV in NO, but it drops to 406.8 eV in di-t-butyl nitroxide.²¹ Since the two t-butyl groups do not appear to contribute much electron density to the nitroxide group in the initial state, it appears that this 3.6 eV shift arises mainly through polarization in the final state. Indeed, electron population calculations based on the RPM model bear this out.²²

In both of these cases core-level binding-energy shifts have been associated with Lewis basicity. Thus, for example, t-butyl iodide appears to be a much stronger base than methyl iodide. This difference appears to arise not through any significant difference in the ionicity of the C - I bonds in the two molecules, but rather because the t-butyl group can more readily accommodate to the loss of an electron, by final-state polarization. While a given t-butyl compound is a stronger Lewis base than is its methyl analogue (e.g. t-butyl alcohol > methanol by 0.82 eV, t-butyl iodide > methyl iodide by 0.63 eV) because of a greater ability to stabilize excess positive charge, t-butyl compounds are also better Brønsted acids because of their greater ability to stabilize excess negative charge, as indicated by Brauman and Blair.¹¹ Final-state polarization also appears to account for the greater speed of substitution of t-butyl alcohol by nucleophilic groups.²¹ In this case the charged "final state" is in fact the transition state of the reaction. The charged carbonium ion is stabilized by polarization in the t-butyl case, thereby lowering the activation energy. We note finally that internal core-level binding-energy shifts among atoms of a given element at different sites in a given molecule would allow the determination of the relative Lewis basicities of these sites, thereby leading to the possibility of predicting which are the reactive sites in the molecule.

V. On Relative Acidities in Solution

From the above comparison of gas-phase proton affinities and core level and lone pair binding-energy shifts it seems very probable that the relative gas-phase acidities of the simple alcohols should vary in the order t-butyl > isopropyl > ethyl > methyl > water, over a range of approximately 1.5 eV. In fact this order was established experimentally by Brauman and Blair,^{10,11} although quantitative comparisons are not yet available. These workers suggested that this gas-phase acidity order arises through internal polarization of the alkyl groups in the ion by the localized charge on the oxygen. In essence this is exactly what we are suggesting to explain the observed values of $\Delta E_B(O\ 1s)$ and $\Delta(PA)$ in these alcohols.

Returning to aqueous solutions, Brauman and Blair attributed the reversal of acidity order to steric hindrance of solvation in the larger alkoxides. They further referred briefly to intramolecular polarizability as a kind of internal solvation,¹¹ which they noted would be smaller than the free energy of solvation in a protic solvent, thus accounting for the reversal of acidity order in water.

We fully concur with this explanation of the acidity reversal. However, since we have approached the problem from a different direction--that of understanding gas-phase core level binding-energy shifts--we find it useful to describe this phenomenon somewhat differently. The O(1s) core-level binding energy in the gas phase decreases with increasing molecular size from H₂O to t-butyl alcohol largely because of extra-atomic relaxation (final-state polarization). Extra-molecular relaxation, or polarization of the surrounding medium, is also possible if the same molecules are studied in solution. This effect would be greatest for the ionization of H₂O and least for t-butyl

alcohol, because the bulky t-butyl group will keep solvent molecules away from at least one side of the -OH group. In going from the gas phase to any solution the O(1s) binding energy of t-butyl alcohol should therefore be increased relative to that of water, and the relative acidity of t-butyl alcohol should be reduced. Thus, whereas Brauman and Blair referred to the final-state polarization as an internal solvation, it is also perhaps useful to consider solvation as augmenting the final-state polarization through polarization of the medium.

Footnotes and References

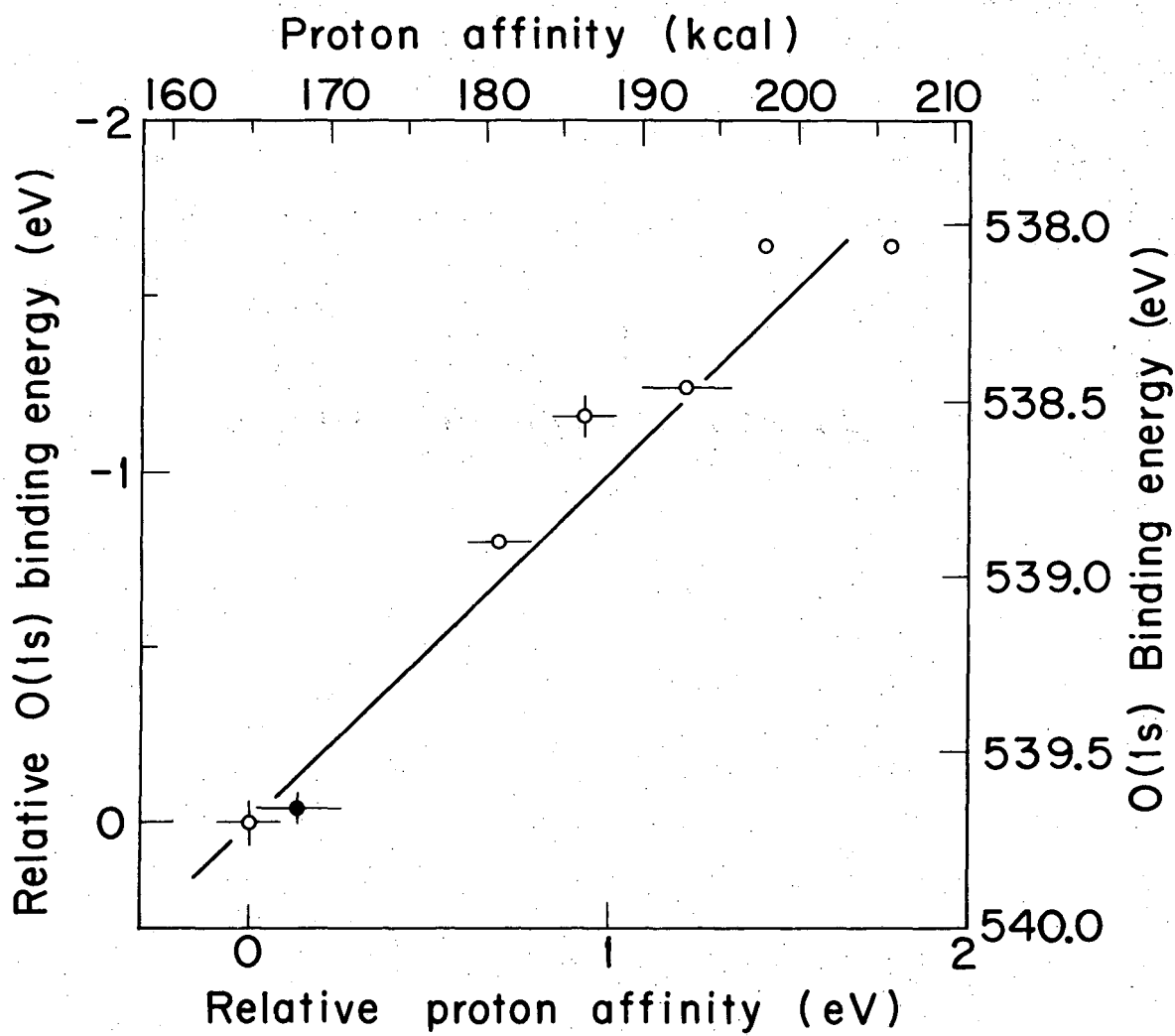
* Work performed under the auspices of the U. S. Atomic Energy Commission.

- (1) R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry (Verlag Chemie GmbH, Academic Press Inc., 1970).
- (2) G. N. Lewis, Valence, Dover Edition (Dover Publications, Inc., New York, 1966), p. 142.
- (3) K. Siegbahn et al., ESCA Applied to Free Molecules (North-Holland Publishing Co., 1969).
- (4) D. W. Davis, M. S. Banna, and D. A. Shirley, *J. Chem. Phys.*, to be published.
- (5) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Am. Chem. Soc.* 94, 6565 (1972).
- (6) See, for example, D. A. Shirley, ESCA, *Adv. Chem. Phys.* 23, 85 (1973).
- (7) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.* 56, 671 (1972).
- (8) D. A. Shirley, *Chem. Phys. Letters* 16, 220 (1972).
- (9) D. W. Davis and D. A. Shirley, *Chem. Phys. Letters* 15, 185 (1972).
- (10) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.* 90, 6561 (1968).
- (11) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.* 92, 5986 (1970).
- (12) J. L. Beauchamp and M. C. Caserio, *J. Am. Chem. Soc.* 94, 2638 (1972).
- (13) J. Long and B. Munson, *J. Am. Chem. Soc.* 95, 2427 (1973).
- (14) D. H. Aue, University of California at Santa Barbara, private communication.
- (15) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.* 10, 378 (1971).
- (16) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.* 94, 4726 (1972).
- (17) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.* 94, 4728 (1972).

- (18) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.* 43, 375 (1971).
- (19) W. C. Price, *Chem. Rev.* 41, 257 (1947).
- (20) J. A. Hashmall, B. E. Mills, D. A. Shirley, and A. Streitwieser, Jr., *J. Am. Chem. Soc.* 94, 4445 (1972).
- (21) D. W. Davis, R. L. Martin, M. S. Banna, and D. A. Shirley, *J. Chem. Phys.*, to be published.
- (22) Reference 21, Table III.

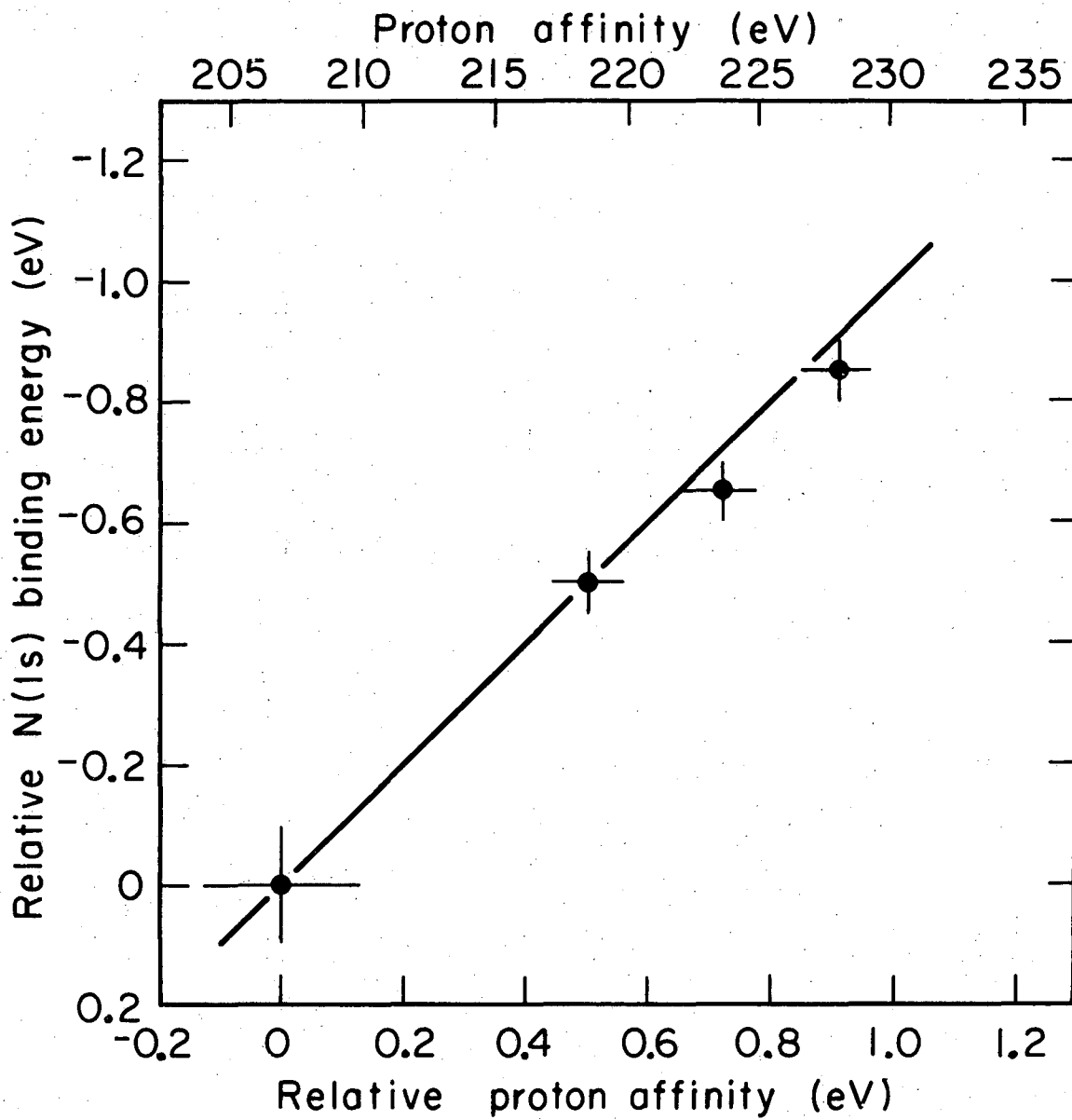
Figure Captions

- Fig. 1. Oxygen 1s binding energies versus proton affinities for simple alcohols (open circles) and $\text{CF}_3\text{CH}_2\text{OH}$ (filled circle), all in the gas phase. Relative $E_B(1s)$ and PA values are referred to H_2O . The values and references are given in Tables I and II. Compounds in order are: H_2O , $\text{CF}_3\text{CH}_2\text{OH}$, methanol, ethanol, isopropyl alcohol, and t-butyl alcohol (for which two values of PA are plotted). The straight line has unit slope and goes through the H_2O point.
- Fig. 2. Nitrogen 1s binding energies versus proton affinities for (from left) NH_3 , methylamine, dimethylamine, and trimethylamine. The PA values plotted are the average of those given in references 16 and 17. The error on the NH_3 point is absolute, while the others are relative. The straight line through the NH_3 point has unit slope.
- Fig. 3. Differences in lone-pair ionization potentials versus differences in calculated relaxation energies for amines (filled circles. From left: NH_3 , methylamine, dimethylamine, trimethylamine) and alcohols (open circles. From left: H_2O , methyl, ethyl, isopropyl, t-butyl alcohol). The straight line has unit slope.
- Fig. 4. Oxygen 1s binding energies in simple alcohols ROH versus iodine $3d_{5/2}$ binding energies in corresponding alkyl iodides RI (from left R = H, methyl, ethyl, isopropyl, t-butyl). The (HI, H_2O) point is taken as a reference and only relative errors on other points are shown. The straight line through the reference point has a slope of unity.



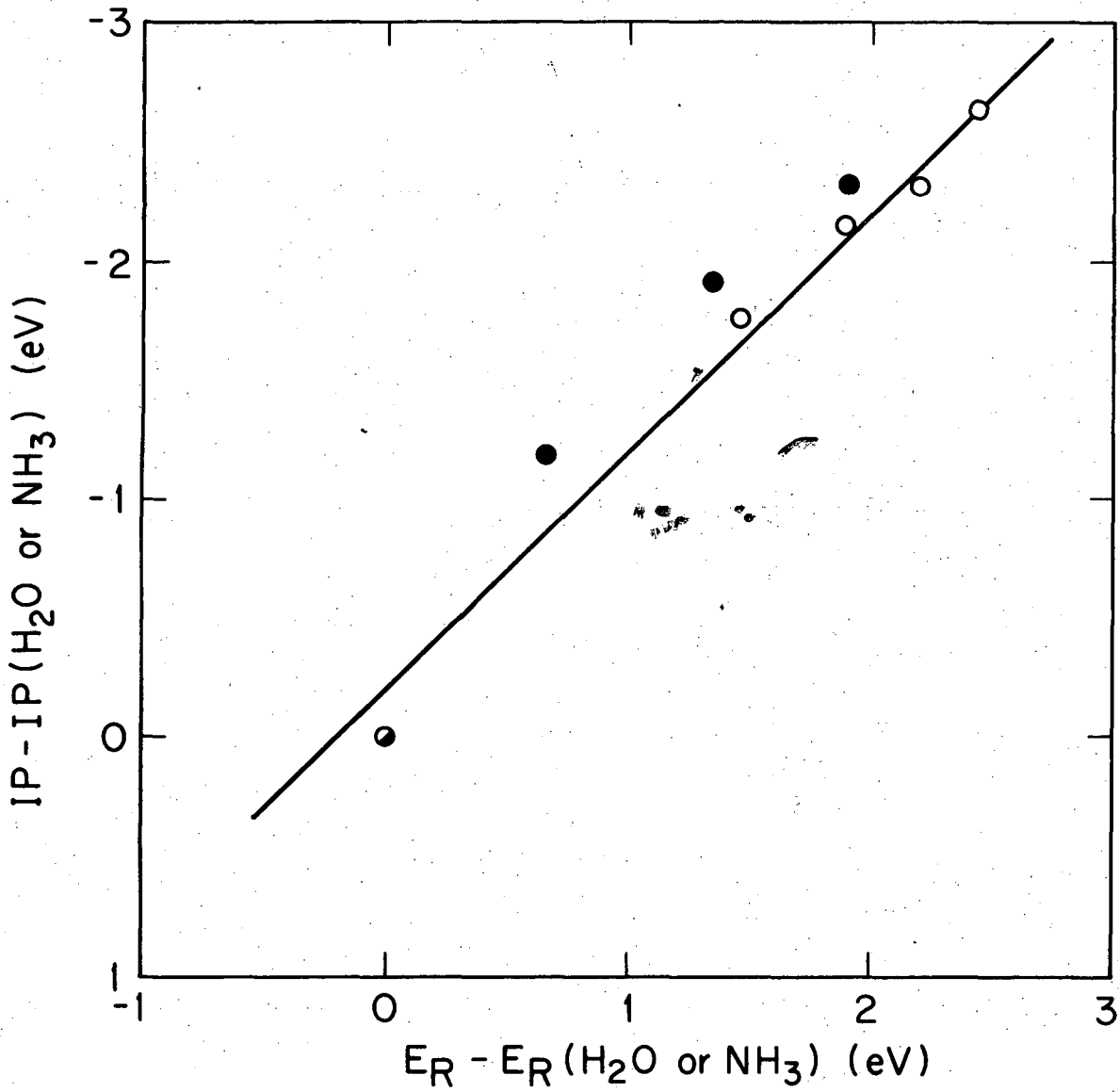
XBL 7312 - 7033

Fig. 1



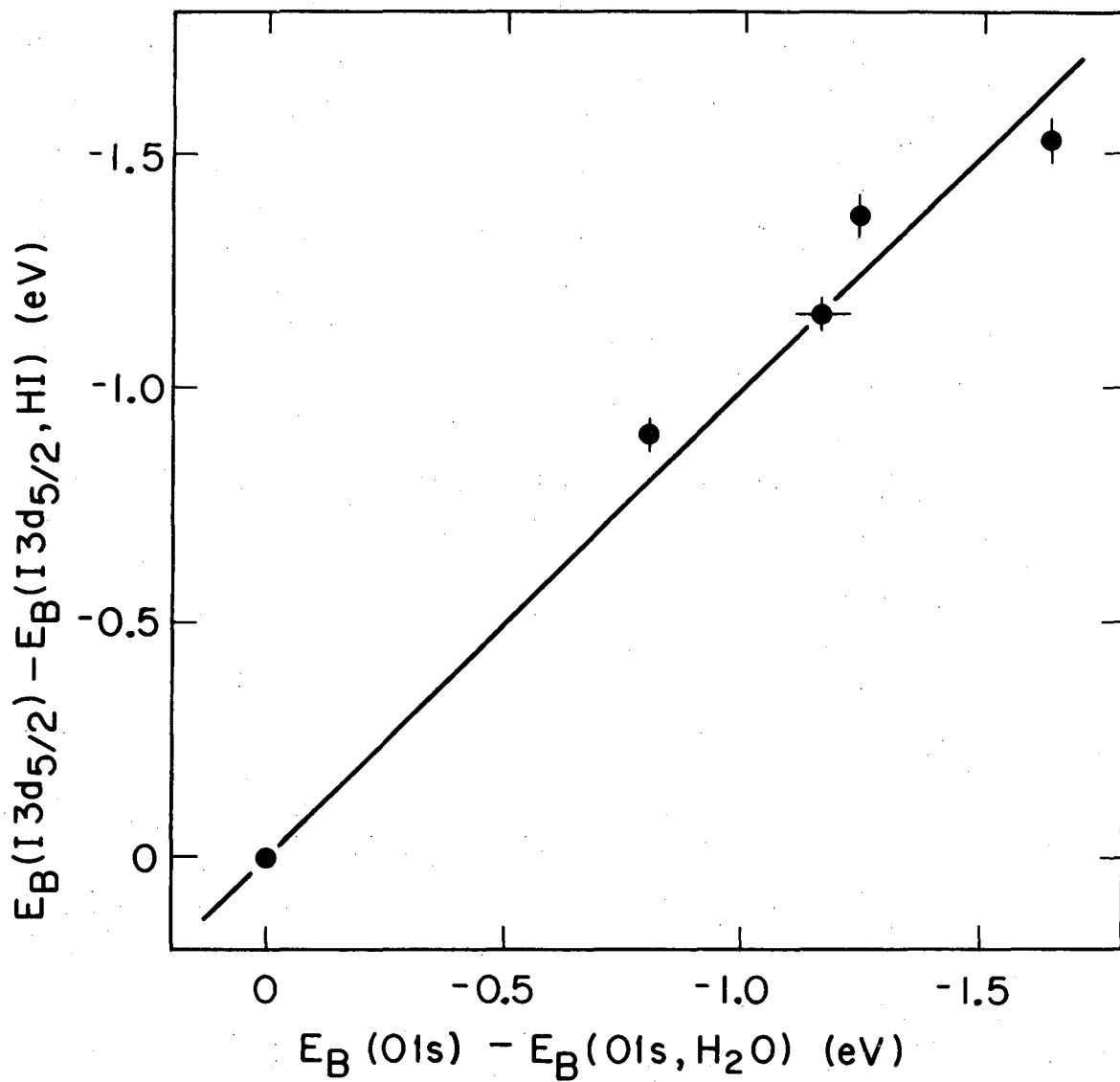
XBL7312-7032

Fig. 2



XBL7312-7031

Fig. 3



XBL7312-7030

Fig. 4

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720