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CORE PHOTOELECTRON SPECTROSCOPY OF SOME ACETYLENIC MOLECULES

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Core Photoelectron Spectroscopy of Some Acetylenic Molecules*

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ABSTRACT

Carbon 1s binding energies have been measured for CH_3CCH, CH_3CCCH_3, CF_3CCH and CF_3CCCF_3 and compared to a verified value for acetylene. Assignments are based on the application of a CNDO potential model with relaxation corrections which is quite successful in predicting binding energy shifts plus qualitative considerations. Substitution of CF_3 groups shifts the acetylenic C_{1s} binding energy from 291.2 (HCCH) to 292.2 in CF_3CCH and 292.7 ev in CF_3CCCF_3 perhaps as a result of electron withdrawal by the CF_3 group from the acetylenic moiety. The unequal differences in shifts are due to a saturation of substituent effect expected in competitive situations. With reservations arising from uncertainties in assignment due to lack of resolution, it appears that acetylenic C_{1s} binding energies decrease (to 290.7 (avg.) in CH_3CCH and to 290.1 ev in CH_3CCCH_3) upon replacement of H by CH_3 groups. It appears that significant portions of these shifts are due to changes in relaxation energy contributions rather than electronic redistributions in the ground state of the molecule. Although the decrease in acetylenic binding energies agrees with the chemical notion that CH_3 groups are electron donating with respect to unsaturated portions of the molecule, the magnitudes of the decrease are much larger than would be expected from ground state electronic polarizations and it is suggested that electron rearrangements (relaxation) following photoionization contribute significantly to the observed shifts. Surprisingly potential and relaxation corrected potential calculations with the CNDO method suggest a large difference in C_{1s} binding energies of the two acetylenic carbon atoms in CH_3CCH which is not verified experimentally nor mirrored by calculations on CF_3CCH. The CH_3 binding energies are 291.8 ev in CH_3CCH and 291.3 ev in CH_3CCCH_3 both higher than values assigned to CH_4 or C_2H_6. The success of relaxation corrected CNDO potentials in interpreting shifts over uncorrected potentials or charge calculations lends further support to its utility.

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INTRODUCTION

It is now well established that core photoelectron spectroscopy (known as ESCA or XPS)[2,3] provides, in the form of chemical shifts of the apparent binding energies, information about the changes of the electronic potentials of atoms accompanying substitution. The most definitive results are obtained on gaseous molecules since in this case the conservation equation

$$h\nu = E_{kin} + E_B \qquad (1)$$

(where $h\nu$ is the energy of the incident photon, E_{kin} the kinetic energy of the ejected electron and E_B the apparent binding energy) is obeyed exactly. Surface effects, charging and contact potential effects which can obscure the variations between molecules do not apply. Since the gaseous sample leaks out and must therefore be continuously replenished, the effect of X-ray induced decomposition following the photoionization process is also eliminated.

Recent contributions to the understanding of the significance and utility of the resultant apparent binding energies obtained by core photoionization studies suggest that they can be analysed in detail to provide chemically useful information. Furthermore, the surface dominated nature of ESCA suggests considerable application to the study of catalytic processes on metal surfaces and the beginnings of such applications have been reported. It is essential for such studies to know the detailed characteristics of the free molecule and we have accordingly embarked on a study of core and valence electron spectroscopy of simple molecules which are of importance as organometallic ligands or in catalytic processes. We report herein core-electron spectra of some acetylenic molecules.

Experimental

Materials: The compounds CF_3CCH, CF_3CCCF_3, CH_3CCH, CH_3CCCH_3 were commercial materials which were used without purification since checking for impurities by both photoelectron spectroscopy and infrared spectroscopy indicated that the materials were greater than 98% pure.

Instrumentation and data processing: The spectra were obtained on the Berkeley Iron Free spectrometer described elsewhere[4,5]. In the present studies the X-ray tube was modified[6] to seal it from the sample compartment and to allow independent pumping of the tube chamber. This modification prevented contamination of the X-ray tube by sample gases and permitted longer periods of operation with good X-ray intensities.

In all cases spectra were obtained with Mg K_α radiation with the sample gas contained in a cell[5] at pressures of the order of 30-100 microns. No pressure dependence of line position (kinetic energy) was found. Data was collected as described elsewhere[4,5] and analysed by means of the program SUNDER[7]. The experimental data were fitted to Gaussian and Lorentzian line shapes characterized by full width at half maximum (FWHM), position and tail parameters. Mg K_α satellites and background were subtracted before deconvolution into components was attempted. The quality of the fit was evaluated by comparing the weighted sum of least square residuals (χ^2) and in general the Gaussian function provided a marginally better fit although in most cases the differences in quality of fit were insignificant. Spectra were obtained for the compound alone for line shape analysis and for an intimate mixture of the sample with argon for calibration against the Ar $2p_{3/2}$ line at 248.62 ev[8]. No significant differences in line shape were observed in the mixed gas experiments. In some cases gases were also calibrated against Neon with comparable results to those obtained with Argon, but all numerical values quoted are obtained with reference to Argon. Line positions are reliable to ±0.1 eV and separations resolved peaks on the same scan are probably good to better than ±0.05 eV.

Results

The results are listed in Table 1 including corrected binding energies (vs Ar $2p_{3/2}$, 248.62 ev), FWHM and relative intensities of all peaks. In the case of fluorocarbons, the fluorocarbon C_{1s} peaks were well separated from the C_{1s} lines of the hydrocarbon moiety. The low resolution of the measurements prevented clear distinctions between the different types of carbons in the case of the hydrocarbon molecules although we have managed in all cases studied herein to distinguish the two major types of carbon atom present in these hydrocarbons. The individual cases are discussed in detail below.

CF_3CCCF_3 There are two C_{1s} lines due to the acetylenic and fluorocarbon moieties separated by 7.25 ev with the acetylenic C_{1s} line appearing to lower binding energy than the CF_3 line and both are clearly resolved. The fluorocarbon line is substantially narrower than the acetylenic C_{1s} line although both peaks enclose nearly equal areas (within experimental error) as expected since the molecule contains equal numbers of atoms of each type.

CF_3CCH The fluorocarbon C_{1s} peak is well separated from the acetylenic carbon peak (7.45 ev) with the acetylenic carbon peak appearing to low binding energy. Although the acetylenic carbon peak is broader than the fluorocarbon peak and it is tempting to associate this width of acetylenic carbon with the fact that two kinds of acetylenic carbon atoms are present, such a procedure cannot be justified because the identical acetylenic carbons in CF_3CCCF_3

also give rise to a peak which is broader than the C_{1s} peak of the fluorocarbon moiety. The comparison of the ratio of the widths of acetylenic C_{1s}/fluorocarbon C_{1s} which is 1.22 in CF_3CCCF_3 and 1.20 in CF_3CCH indicates clearly that two kinds of carbon cannot be distinguished in the acetylenic C_{1s} line of CF_3CCH. The very small predicted difference between these two carbons (vide infra) supports the experimental indistinguishability within experimental error, the areas of $C_F/C_{acetylenic}$ carbon types are 1/2 in agreement with the molecular formula.

CH_3CCCH_3 There are two carbon environments clearly indicated in the spectrum although the resolution is incomplete (Fig. 2). The spectrum can be separated into either (a) two components of equal area but different width (FWHM values 1.27 and 1.13 ev respectively) or into (b) two components of equal width in which case each component peak has a different area (Ratio 0.80/1). Comparison of the quality of the two analyses based on the weighted χ^2 values indicates that a marginally better fit is obtained from the fixed FWHM analysis. When both FWHM and area were allowed to run free, no satisfactory solution was obtained. Since neither the data nor the analysis procedure indicate clearly whether fixed FWHM or fixed area are preferable we select the solution in which the relative areas are constrained to be equal reflecting the equality of the numbers of each type of carbon in the molecule in preference to the alternative with no significant sacrifice of the χ^2 criterion. The solution is then consistent with that of the perfluorinated analog, CF_3CCCF_3.

$\underline{CH_3CCH}$ The presence of different carbon environments in this molecule is indicated only by the asymmetry of the C_{1s} peak (Fig. 2) but it is possible and justified by the facile resolution of the C_{1s} peak of CH_3CCCH_3 to divide this asymmetric peak into at least two components of 1:2 intensity ratio. Since the carbon types are not clearly distinguished experimentally, the major emphasis was placed on a deconvolution with a fixed 2:1 area ratio in keeping with the atomic ratios within the molecule. This procedure gave two peaks with a separation of 1.14 ev and different width. The narrowest of the peaks (FWHM 1.12 ev) is the unit area peak which we will assign to the methyl carbon. On a more speculative level resolution of three equal area components (at equal FWHM) gave an equally good fit to the data and preserved the area and position of the previously extracted unit area peak which we wish to assign to the methyl carbon. A good three component deconvolution resolution was achieved with only fixed FWHM throughout. Attempts to allow free FWHM for the acetylenic carbon gave nonsensical results. The positions of all three components are in reasonable, but not exact, agreement with predictions.

<u>Acetylene</u>: The core and molecular orbital spectra of the simplest molecule of the series was reinvestigated and the resultant energies found to be in good agreement with those published elsewhere[9]. The valence level spectra were of significantly better quality (Fig. 3) than those obtained elsewhere[9] as a result of the modifications to the system which improved the lifetime of the X-ray tube in the presence of gases. It is notable however that the weak π orbitals

were still not observed. The C_{1s} binding energy obtained herein, 291.14 ev (calibrated vs Ar $2p_{3/2}$ which has been revised recently[8] to 248.62 ev) is in excellent agreement with the earlier value (291.2 ev)[9]. The valence band levels are found at 23.33 and 18.59 ev in agreement with 23.5 and 18.5 reported by Thomas[9]. The two peaks have respective relative areas of 1.106/1 and FWHM of 1.53 and 1.91 ev respectively when fitted to a Gaussian line shape function.

Discussion

Carbon (1s) Apparent Binding Energies:

Assignments are straightforward in the cases of CF_3CCCF_3 and CF_3CCH. The low binding energy C_{1s} lines are clearly the acetylenic carbons and the higher binding energy lines are due to the C_{1s} of the fluorocarbon fragments in keeping with the expected shift of C_{1s} to higher binding energy as a result of electron withdrawal from carbon by fluorine. In both fluorocarbon molecules the acetylenic carbon binding energies are also shifted to higher binding energy values (about 1.0 and 1.5 ev for CF_3CCH and CF_3CCCF_3 respectively) relative to the binding energy in the parent HCCH molecule. This shift to higher binding energy is expected as a result of the electron withdrawing ability of the CF_3 group which increases the positive charge on the acetylenic carbon atoms.[3] It is notable that two CF_3 groups are not twice as effective as one indicating that such substitutional effects are not directly proportional to the number of substituent groups. This "saturation of substituent effect " is probably a major reason for the difficulty of creating unique substituent contribution scales. Exactly proportional effects are not to be expected if we consider that the single CF_3 in CF_3CCH is able to withdraw electron density from two acetylenic carbons (and appears to do so since the two acetylenic carbons in CF_3CCH are indistinguishable), whereas the two CF_3 groups in CF_3CCCF_3 must compete with each other for the electron density available on the acetylenic carbon atom and must therefore be individually less successful at withdrawing electron density. All competitive effects are likely to behave in a similar fashion.

Assignment of C_{1s} binding energies in the hydrocarbons is less straightforward because the shifts are not sufficient to provide complete resolution under the limitations of soft X-ray excitation. However there are clearly two different carbon peaks in CH_3CCCH_3 which can be easily separated by curve fitting techniques. The resultant two peaks, constrained to have equal areas in the absence of evidence to support any other desirable constraint can be assigned in two possible ways: (a) the lower binding energy component at 290.1 ev can be assigned to the acetylenic carbons and the higher at 291.3 ev to the methyl carbons or (b) the reverse which gives the acetylenic carbon a slightly higher binding energy than for acetylene itself.

We prefer the former assignment for a variety of reasons, none of which are unfortunately very substantial. The peak at higher binding energy is narrower than that at lower energy and since the acetylenic peaks appear to be broader than either fluorocarbon or saturated hydrocarbon peaks, we prefer to associate the broader, lower energy peak to the C≡C grouping. Further Thomas' data[9] suggests that replacement of H by CH_3 causes a shift to lower binding energy (i.e. opposite to the effect of CF_3 above) thus C≡C in CH_3CCCH_3 should have lower binding energy than in acetylene as suggested by assignment (a). The C⋮C group is thus acting to withdraw charge from the CH_3 group and causes a shift to higher binding energy since the C_{1s} binding energy of the CH_3 group in CH_3CCCH_3 is larger than in CH_4 under assignment (a). This is in keeping with chemical expectation[10] and the trends established elsewhere[9], however it does not permit this work to independently indicate trends of chemical interest. Furthermore it must be pointed out that the linewidths obtained for this molecule may be artefacts of the data analysis and not genuine. Also of concern is the fact that the estimated relaxation energies change substantially from CH_4 to a CH_3 group and from HCCH to a substituted acetylene hence it is questionable whether the data for a substituted molecule can be compared with the parent. Fortunately, however, calculations of changes in atomic potential and relaxation effects using the CNDO model (vide infra) also support assignment (a) and in fact provide the most substantial support for our assignment.

The final assignment to be made, that for CH_3CCH, is the most difficult of all because the differences in carbon shifts are the smallest encountered and up to three carbon environments must be considered possible. A shoulder on the high binding energy side indicates the presence of a distinguishable component in the major peak and a peak can be easily extracted by curve fitting procedures. We have constrained this peak to unit area and assign it to the CH_3 carbon atom following the assignment made above for CH_3CCCH_3. Thus this unit intensity peak which possesses a relatively narrow linewidth gives a consistent shift of CH_3 C_{1s} binding energy to a higher value than that for CH_4, a result which is consistent with donation of electron density to the unsaturated part of the molecule by the CH_3 group as suggested above for CH_3CCCH_3 and also elsewhere[10]. The same arguments therefore result in a compatible assignment of both CH_3CCH and CH_3CCCH_3. The remaining area of 2 units in the peak can only arise from the two acetylenic carbon atoms in CH_3CCH. The indistinguishability of the two acetylenic carbon atoms in CF_3CCH noted above however suggests that there may not be any justification for making a distinction between the different acetylenic carbon atoms in CH_3CCH and we should proceed no further with peak deconvolution procedures. Since the potential model calculations discussed below do indicate a large and possibly distinguishable difference between these two acetylenic carbon atoms in CH_3CCH, deconvolution of this two fold intensity component into two unit area components which could therefore be associated with each of the acetylenic carbon atoms was successfully attempted yielding three equal area (intensity) peaks in reasonable positions but only when linewidths were constrained to be equal to that of the CH_3 group peak (Table) and therefore the separability of the components may not be real. One of the resultant three peaks corresponded identically to the peak extracted from the high binding energy side during the analysis discussed above in which the area ratio of the components was fixed at 1:2. This unique high binding energy peak is reasonably assigned to the carbon atom of the methyl group, consistent with the assignment made for the 1:2 area ratio case. The acetylenic carbon atoms can be assigned to the two components of lower binding energy thus providing a consistent assignment within the hydrocarbon series. The separation of the two C_{1s} binding energies obtained in this manner is in fair agreement with the calculated (CNDO) separation. Since no inflections were observed in the two fold intensity portion of the peak, it is difficult to justify the reality of the two acetylenic C_{1s} values obtained by curve analysis and the results of the deconvolution procedure may not correspond to reality. The results of the second analysis should be treated with scepticism.

CNDO Potential Model Calculations and Predictions of Shifts

In a series of selected molecules of this type the magnitudes of atomic potential changes cannot be evaluated from qualitative considerations of atomic number or oxidation state. Thermochemical approaches, although elegant and useful, are difficult to apply to complex molecules because of limitations to the available thermodynamic data. It is therefore useful to have a method of estimating nuclear potentials which correlate with observed binding energies and such a method has been described by Davis and Shirley[11] utilizing a slightly modified CNDO approach. Relaxation effects can be estimated by the simple technique of exchanging the central core for the element of one higher unit of nuclear charge[11] whereupon the relaxation energy is given by

$$E_R = 1/2\ V(Z+1) - 1/2\ V(Z) \tag{2}$$

where V(Z) is the calculated atomic potential for the nucleus of charge Z and V(Z+1) is the resultant potential obtained upon substitution of the nucleus of Z+1 charge in the molecule following the "equivalent cores"[12] approach to relaxation potential calculations. Binding energies can be predicted relative to a standard from either the change in nuclear potential:

$$\Delta E_B = -\Delta V(Z) \tag{3}$$

which is the Ground State Potential Model (GPM)[11] or by the more accurate relationship

$$\Delta E_B = -1/2\ V(Z) - 1/2\ V(Z+1) \tag{4}$$

which includes relaxation contributions (The Relaxation Potential Model, RPM)[11]. Predictions based on (4) are more successful because the relaxation contributions are relatively large (about 10% of the nuclear potential effect) and are dependent on molecular complexity.[11] In a series of similar molecules with similar numbers of atoms (e.g. CX_4 molecules) the relaxation contributions are likely to be similar and the binding energy shifts may be obtained directly from the computed changes in nuclear potential which arise from substitution because the errors involved in the neglect of relaxation effects will be small. Chemically interesting studies, however, usually involve interchanging substituents of various type and complexity on the same framework with a resultant variation in molecular size. In such cases the relaxation effects can be substantially different from one molecule to another (perhaps as much as 2 ev or more) and apparent binding energy shifts will not directly reflect the effect of a substituent on the nuclear potential at the atom under observation but rather the combined effect of this change in nuclear potential and the change in relaxation properties of the molecule (and its ion) relative to those of the series prototype.

The relationship between RPM atomic potentials[11] with observed binding energies are plotted in Figure 4 using an arbitrary potential scale. Predicted and calculated ΔE_B shifts relative to HCCH are shown in Figure 5. The agreement is quite good and the points are in good agreement with the line of unit slope in Fig. 5. As expected GPM predictions were considerably less successful than RPM predictions and are not shown graphically although the data is given in the Table. Alternative predictions from calculated atomic charges are not nearly as successful as either GPM or RPM models and considerable scatter resulted when such charges were plotted against binding energy shifts. CNDO and similar approximate methods are not likely to provide good estimations of charge hence the lack of agreement is not surprising.

Both GPM and RPM CNDO models[11] predict the differences in C_{1s} binding energies between CF_3 or CH_3 and acetylenic carbon atoms quite well for both fluorocarbons and for CH_3CCCH_3. The predicted separations are best for the relaxation potential model but are reasonably good for the GPM model, which is not too surprising because differences in atomic potentials of atoms in the same molecule are probably more accurate as a result of cancellation of errors inherent to the model. Since the RPM model accounts for changes in both atomic potential and the relaxation contribution it is not too surprising, perhaps, that this model provides a better prediction of observed shift.

The predicted shifts and separations support the assignments for CF_3CCCH_3, CF_3CCH, CH_3CCH and CH_3CCCH_3 made above. Notably the calculations support the assignment of CH_3 C_{1s} to the peak of higher binding energy in the latter providing the best independent support for the assignment preferred above. Some comment on the calculations and assignments in CH_3CCH is however warranted because of the surprisingly large differences predicted between the two acetylenic carbon atoms in this molecule. Calculations with either the GPM or RPM models using CNDO methodology support the assignment of the highest binding energy peak as the C_{1s} of CH_3. This is the peak which appears as a shoulder to high binding energy and can be easily extracted by deconvolution techniques. The trend in CH_3 and C≡C C_{1s} binding energies with substitution (vide infra) is in agreement with this assignment. The calculations, however, suggest that there is a substantial difference in C_{1s} energies, of the order of 1.7 ev, of the two different acetylenic carbon atoms with the carbon bearing the single hydrogen appearing to lowest binding energy regardless of the model or whether the pp' or point charge approaches are used.[11] No firm experimental evidence is available to suggest that the observed C_{1s} line should be separated into more than the methyl C_{1s} binding energy peak of unit area and an acetylenic carbon peak of twofold area ratio but the double area peak can be divided into two equal area components by deconvolution procedures. Alternatively, the unit area peak at high binding energy obtained in both analyses might be more suitably associated with the ≡C-H acetylenic carbon, since the predicted separation of $\underline{C}H_3$ and $CH_3-\underline{C}$ C_{1s} lines is very small (<0.5 ev). That assignment is in conflict with the binding energy predictions successful in all other molecules discussed herein and in numerous other cases [11] which clearly give the CH_3 C_{1s} binding energy the highest and the ≡C-H C_{1s} binding energy the lowest value in keeping with our favoured assignment. Perhaps the CNDO method fails to estimate the carbon potentials correctly in CH_3CCH, which is an unsymmetrical molecule, but it is difficult to accept such a failure when similar calculations on CH_3CCH do not indicate a similar difference between the acetylenic carbon atoms. Furthermore, the experimental evidence also indicates no great differences in acetylenic C_{1s} binding energies in either CF_3CCH or CH_3CCH. In the case of CF_3CCH computed atomic potentials (GPM) and relaxation energies of each acetylenic carbon atom are very similar and the resultant binding energy difference between these carbon atoms is very much smaller than resolution capability whereas we might have naively expected a larger difference between the acetylenic carbon atoms in this case because of the greater electron withdrawing effect of the CF_3 group. In contrast, the potentials (GPM) at each carbon atom in CH_3CCH are substantially different, predicting that binding energies decrease in the order $\underline{C}H_3 > CH_3\underline{C}\equiv > \equiv\underline{C}H$ with 0.8 - 1.0 ev difference between each type of carbon. Furthermore, the relaxation energies for the potentially different acetylenic carbon atoms of CH_3CCH are substantially different (E_R for CH_3, 16.34, for $CH_3\underline{C}\equiv$, 15.88 and for $\equiv\underline{C}H$, 16.73 ev) in contrast to the nearly identical relaxation energies obtained (E_R for $CF_3\underline{C}\equiv$, 16.40 $\equiv\underline{C}H$ 16.73 ev) for the acetylenic carbon atoms of CF_3CCH. Thus for CH_3CCH one acetylenic carbon atom has the smallest and the other the largest relaxation energy with the relaxation energy of the carbon atom in the methyl group possessing an intermediate value. Since the potentials increase (and thus predicted E_B decreases) in the order $CH_3 > CH_3\underline{C}\equiv > \equiv\underline{C}H$ addition of this unequal relaxation contribution tends to make the difference between the $\underline{C}H_3$ and the $CH_3\underline{C}\equiv$ binding energies smaller than the potential (GPM) result alone would predict and simultaneously makes the difference between the two types of acetylenic carbon atoms greater than the potential model suggests. The result is a suggestion of possible resolution which is not experimentally observed. It would be of interest to reinvestigate the C_{1s} spectra of

CH_3CCH under significantly greater resolution to establish if these two acetylenic carbons are indeed as different as indicated by computation, however we suspect that the result is an artefact of the computational model and true relaxation effects are distributed more evenly throughout the molecule.

The relaxation energies (E_R) given in Table 1 which are estimated from equation (2) illustrate the varying contributions from the different types of carbon and the influence of molecular complexity. It is notable that the range of E_R for a <u>given type</u> of carbon is nearly 1 ev even within the limited series of molecules considered herein, indicating the necessity for including relaxation contributions in any prediction of binding energy shifts as concluded above. Also notable is the larger magnitude of relaxation contributions from the acetylenic portion of the molecule compared to either the CH_3 or CF_3 portions of the molecule, the <u>difference</u> being about 1 ev. Furthermore, relaxation contributions to the acetylenic C_{1s} binding energy of the substituted acetylenes are about 1 ev larger than for acetylene itself. All these differences serve to emphasize the necessity for including relaxation effects in predictions of binding energies since relaxation effects appear to contribute a significant proportion of the observed shifts. It is notable that the ground potential model[11] suggests smaller differences than are observed for CH_3 substitution and larger differences than are observed for CF_3 substitution whereas the relaxation model[11] predictions are closer to the observed shifts. The efficacy of the relaxation model presumably arises from the ability of this model to account for the dynamic polarization effects (electron relaxation) following photoionization from inner core levels. These relaxation contributions obviously vary with the complexity of the molecule and may therefore provide a means of establishing atomic and/or groups polarizabilities which might be important for the understanding of chemical reactivity since electronic reorganization effects are undoubtedly important in the formation of a transition state. It is important to emphasize that these relaxation energies are not directly measurable quantities since we cannot observe photoionization to the unrelaxed ion with a core electron vacancy.

In the present case it seems that replacement of H by CH_3 or CF_3 in acetylene increases the relaxation contribution of the acetylenic portion of the molecule (and also the relaxation contribution of the CX_3 portion of the molecule vs the CX_4 precourser[11]) presumably as a result of greater redistributions of electron density following photoexcitation in the substituted molecules. There is however no clearly defined association of the relaxation energy differences with changes of substituent and it is probably unreasonable to expect that these effects can be exclusively apportioned to segments of the molecule since the entire molecule is probably involved in the dynamic electronic redistributions which are described crudely by the relaxation process. It would be of interest however to investigate the utility of this model with regard to further understanding of intramolecular relaxation and its importance in chemical reactivity. Furthermore, it is clear that the observed binding energy shifts include relaxation effects (arising from dynamic electronic redistributions) as well as a static contributions arising from the modification of atomic potentials in a molecule as a result of substitution of atoms or groups with different inductive effects on the molecular framework, the actual binding energy shifts themselves may be of great importance in the study of substituent effects on chemical reactivity.

Summary and Conclusions:

Substitution on CF_3 on an acetylene framework induces a shift in binding energy of the acetylenic carbon to higher values whereas substitution of CH_3 induces a shift to lower E_B values. Although these shifts are in keeping with the trend expected from a consideration of changes in nuclear potential at the acetylenic carbon atom as a result of substitution of electron withdrawing (CF_3) or electron donating (CH_3) substituents, it is clear that the relaxation energy makes substantial contributions since the shifts and separations are better predicted by a model which includes corrections for the relaxation effects. A correlation diagram (Fig. 6) illustrates the trends proposed. It is perhaps surprising that the effects of methyl substitution are as large as indicated and it must be remembered that alternative assignments (which are however not supported by the CNDO predictions or experimental evidence) could be made which would destroy or deemphasise the trends. The assignments appear to be correct and serve to emphasize that substitution may have an unexpectedly large effect which is only partly related to the ground state behaviour of the molecule since there is a significant contribution to the observed binding energy shifts from the electronic structure of the ion which is in general different from that of the molecule. These relaxation effects, which arise from rearrangement of extranuclear electrons following photoionization, appear to reflect atomic and/or group polarizabilities in the molecule. They are not at present clearly separable into group or atomic contributions. The RPM model appears to account rather well for the observed shifts because it accounts for electronic reorganizations in the molecule. The surprisingly large differences in calculated potentials in CH_3CCH which are not paralleled in CF_3CCH is deserving of further investigation since they may be an artefact of the computational model.

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TABLE 1

CALCULATED AND EXPERIMENTAL BINDING ENERGY VALUES

Molecule	Atom Type	$-[V(Z)]$ GPM ev	$-[V(Z+1)]$ ev	$-[\frac{1}{2}V(Z)+\frac{1}{2}V(Z+1)]$ RPM ev	$\frac{1}{2}V(Z+1)-\frac{1}{2}V(Z)$ E_R ev	ΔE_B(calc) (GPM) ev	ΔE_B(calc) (RPM) ev	$E_B{}^a$(FWHM)^b ev		ΔE_B(exp) ev vs HCCH	
HCCH	$\underline{C{\equiv}C}$	89.27	120.42	104.85	15.58	0	0	291.14(1.28)		0	
CH_3CCCH_3	$\underline{C}H_3$	88.23	121.27	104.75	16.52	+1.04	+0.10	291.3_0(1.13)		+0.18	
	$\underline{C{\equiv}C}$	89.36	123.14	106.25	16.89	-0.09	-1.40	290.0_3(1.27)		-1.06	
	Separation				-	(1.13)	(1.50)	(1.27)		-	
CH_3CCH	CH_3	88.10	120.78	104.44	16.34	+1.17	+0.41	$291.7_7{}^c$(1.16)^d	$291.7_7{}^c$(1.17)	+0.63	+0.63
	$-\underline{C}{\equiv}C-$	88.93	120.68	104.81	15.88	+0.34	+0.04	$291.0_7{}^c$(1.16)^d	$290.7_3{}^e$(1.45)	-0.07	-0.41
	Separation				-	(0.83)	(0.37)	(0.70)		-	
	$-C{\equiv}\underline{C}H$	89.86	123.31	106.59	16.73	-0.59	-1.74	$290.4_0{}^c$(1.16)^d		-0.74	
	Separation				-	(0.93)	(1.78)	(0.57)	(1.04)	-	-
CF_3CCCF_3	$\underline{C}F_3$	79.73	111.74	95.74	16.01	+9.54	+9.11	299.9_8(1.19)		+8.84	
	$\underline{C{\equiv}C}$	86.07	120.95	103.16	17.09	+3.20	+1.69	292.7_3(1.38)		+1.59	
	Separation		-		-	(6.34)	(7.42)	(7.25)		-	
	$\underline{F}$	250.49	300.32	275.41	24.92	-	-	694.5_4(1.83)		-	
CF_3CCH	$\underline{C}F_3$	80.41	111.99	96.20	15.79	+8.86	+8.65	299.7_0(1.28)		+8.56	
	$\underline{C}{\equiv}CH$	87.50	120.29	103.90	16.40	+1.77	+0.95	292.2_4(1.45)		+1.10	
	$C{\equiv}\underline{C}H$	87.47	120.55	104.10	16.63	+1.80	+0.75				
	Sep CF_3-$C\underline{C}$(avg)		-		-	(7.08)	(7.80)	(7.46)		-	
	$\underline{F}$	251.17	300.65	275.91	24.74		-	694.7_5(1.86)		-	
Fluorine E_B shift (CF_3CCH-CF_3CCCF_3)					-	(0.68)	(0.50)	0.21^f		-	

---

a Values are reliable to about ±0.05, separations to ±0.02 ev.

b Gaussian full width half-maximum

c Unit area peak

d This parameter fixed throughout series

e Area of peak is 2 units, fixed relative to unit area peak

f Experimental difference

Figure Captions

Fig. 1. Gas phase spectrum of CF_3CCCF_3 and CF_3CCH at pressures of 40 and about 60 μ respectively. The experimental data is shown as point symbols (+) and the calculated spectrum using a Gaussian line shape function is shown as a solid line. Satellites of MgK_α radiation are shown on calculated line shapes and are subtracted from other components where necessary. The corrected binding energies were obtained from calibration with Argon as described in the text.

Fig. 2. Observed and calculated electron spectra of CH_3CCCH_3 and CH_3CCH obtained at an experimental pressure of about 50 μ. Observed data are given as point symbols (+) with the vertical height of the symbol indicating the relative error of the measurement. Computed lineshapes were derived assuming a Gaussian line shape function with <u>total</u> <u>area</u> ratios fixed as indicated. The corrected energy scale was obtained by calibration with an intimate mixture of argon as described in the text.

Fig. 3. Valence level spectra of HCCH at a pressure of 100 μ excited with MgK radiation. Experimental data are given by point symbols (+) with the vertical height of the symbol reflecting the error in the data. Lineshapes were fitted with Gaussian functions and satellite peaks were subtracted as indicated. The corrected energy scale was obtained by calibration with Argon.

Fig. 4. Binding Energy (E_B) <u>vs</u> the nuclear potential corrected for relaxation contributions. The points correspond to the molecule and atom indicated. The point 3d represents the average of the computed potential of the two acetylenic carbon atoms in CH_3CCH plotted against the experimental C_{1s}

binding energy obtained if these carbon atoms are considered to be indistinguishable. The line represents the best straight line fit to the data using the point 3d rather than 3b and 3c for CH_3CCH.

Fig. 5. Predicted and observed binding energy shifts relative to C_{1s} of HCCH. The line is constrained to unit slope. Point 3d represents the average computed shift of the two acetylenic carbon atoms in CH_3CCH and is compared to the experimental binding energy shift obtained for indistinguishable carbon atoms.

Fig. 6. A correlation of C_{1s} binding energy with carbon environment. Two alternatives are shown for CH_3CCH (a) the case where acetylenic carbon atoms are considered indistinguishable and fitted by one Gaussian peak of two fold intensity and (b) the less defensible case where two C_{1s} energies have been extracted from the two fold area peak above by line shape analysis. Either alternative is compatible with a regular correlation with substitution.

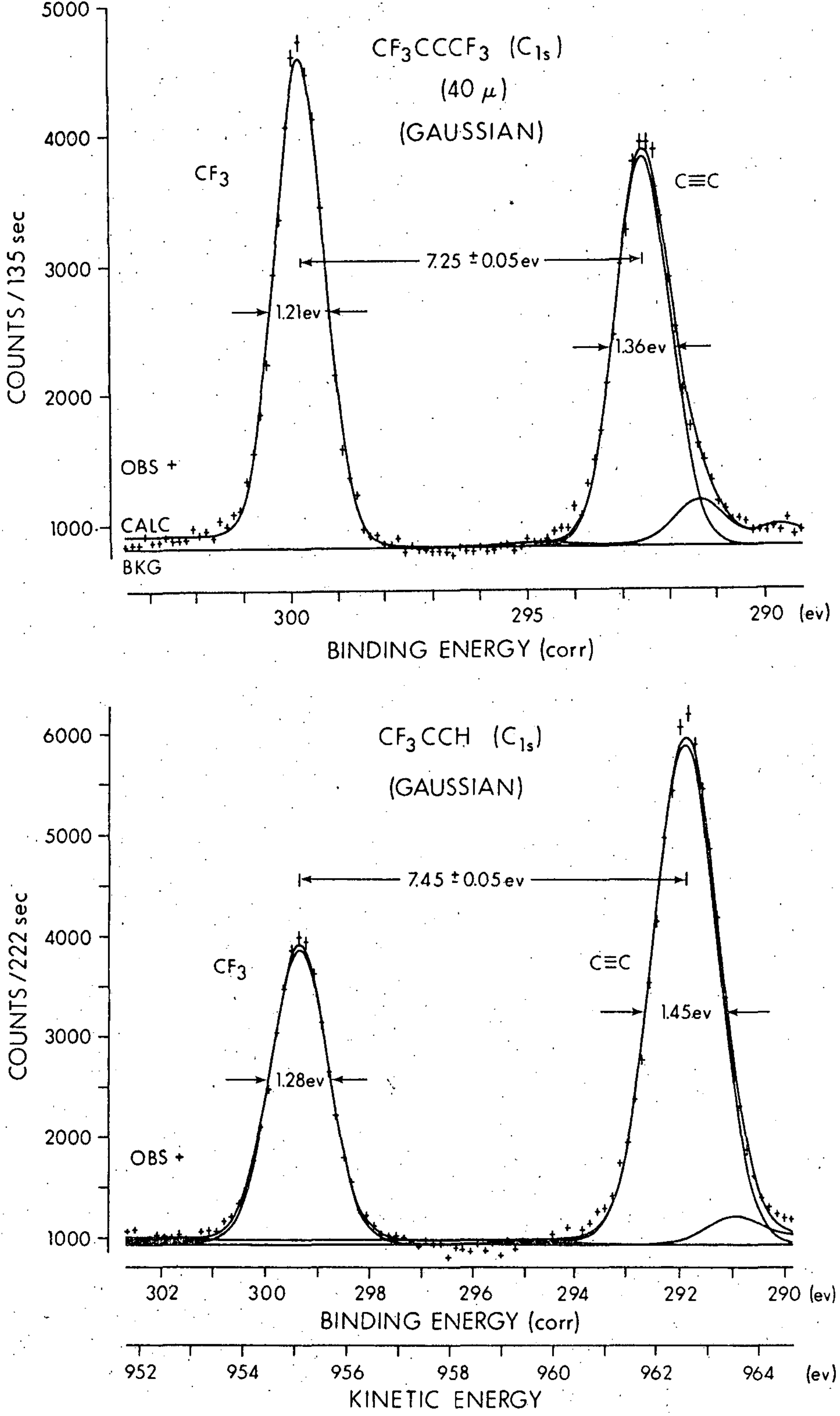
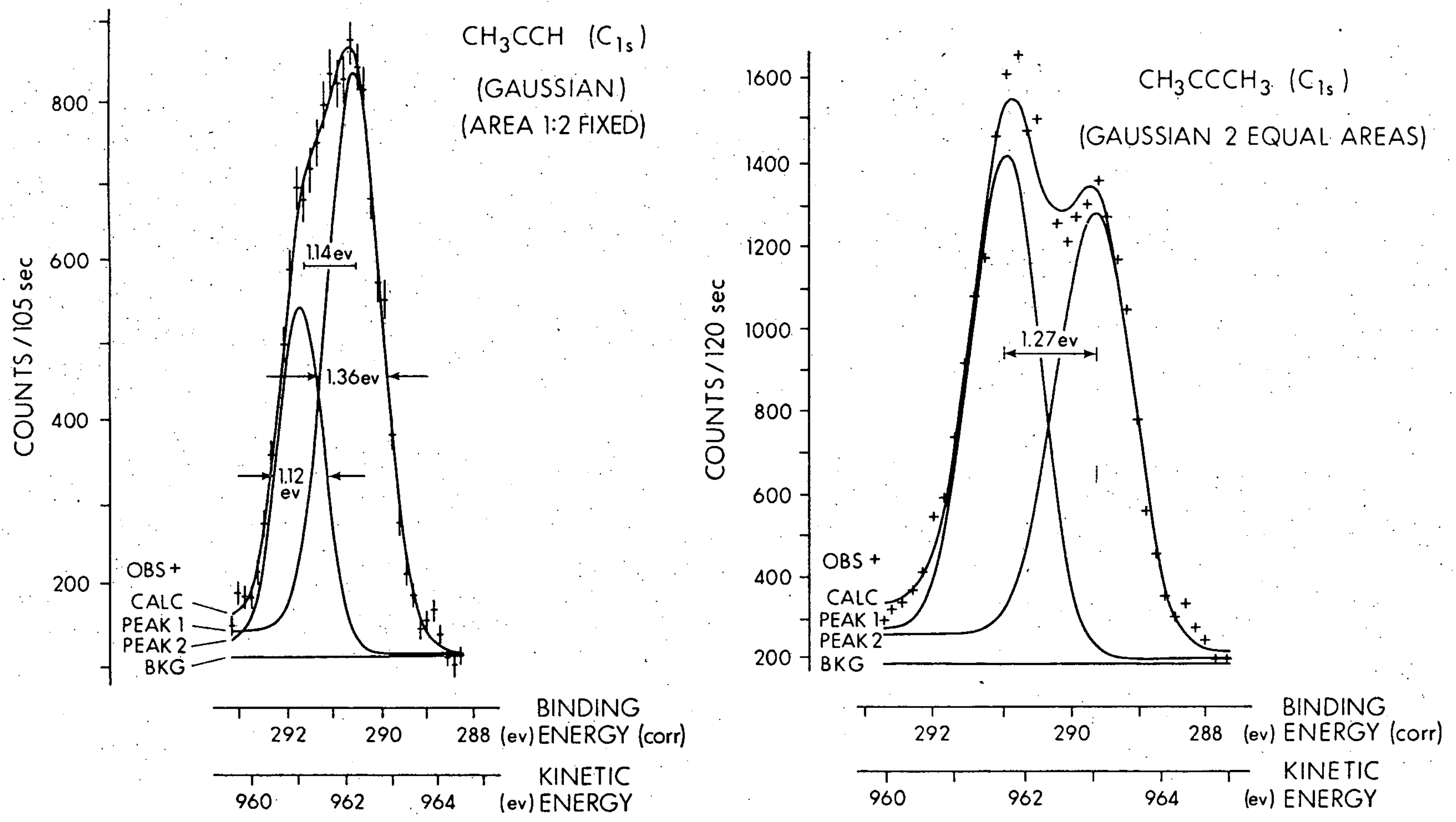

CF3CCCF3 (C1s)
(40 μ)
(GAUSSIAN)
CF3
C≡C
7.25 ± 0.05ev
1.21ev
1.36ev
OBS +
CALC
BKG
COUNTS / 135 sec
5000
4000
3000
2000
1000
300
295
290 (ev)
BINDING ENERGY (corr)
CF3CCH (C1s)
(GAUSSIAN)
7.45 ± 0.05ev
CF3
C≡C
1.45ev
1.28ev
OBS +
COUNTS /222 sec
6000
5000
4000
3000
2000
1000
302
300
298
296
294
292
290 (ev)
BINDING ENERGY (corr)
952
954
956
958
960
962
964
(ev)
KINETIC ENERGY

Fig. 1



CH$_3$CCH (C$_{1s}$)
(GAUSSIAN)
(AREA 1:2 FIXED)
COUNTS / 105 sec
800
600
400
200
1.14 ev
1.36 ev
1.12 ev
OBS +
CALC
PEAK 1
PEAK 2
BKG
BINDING (ev) ENERGY (corr)
292
290
288
KINETIC (ev) ENERGY
960
962
964
CH$_3$CCCH$_3$ (C$_{1s}$)
(GAUSSIAN 2 EQUAL AREAS)
COUNTS / 120 sec
1600
1400
1200
1000
800
600
400
200
1.27 ev
OBS +
CALC
PEAK 1
PEAK 2
BKG
BINDING (ev) ENERGY (corr)
292
290
288
KINETIC (ev) ENERGY
960
962
964

Fig. 2.

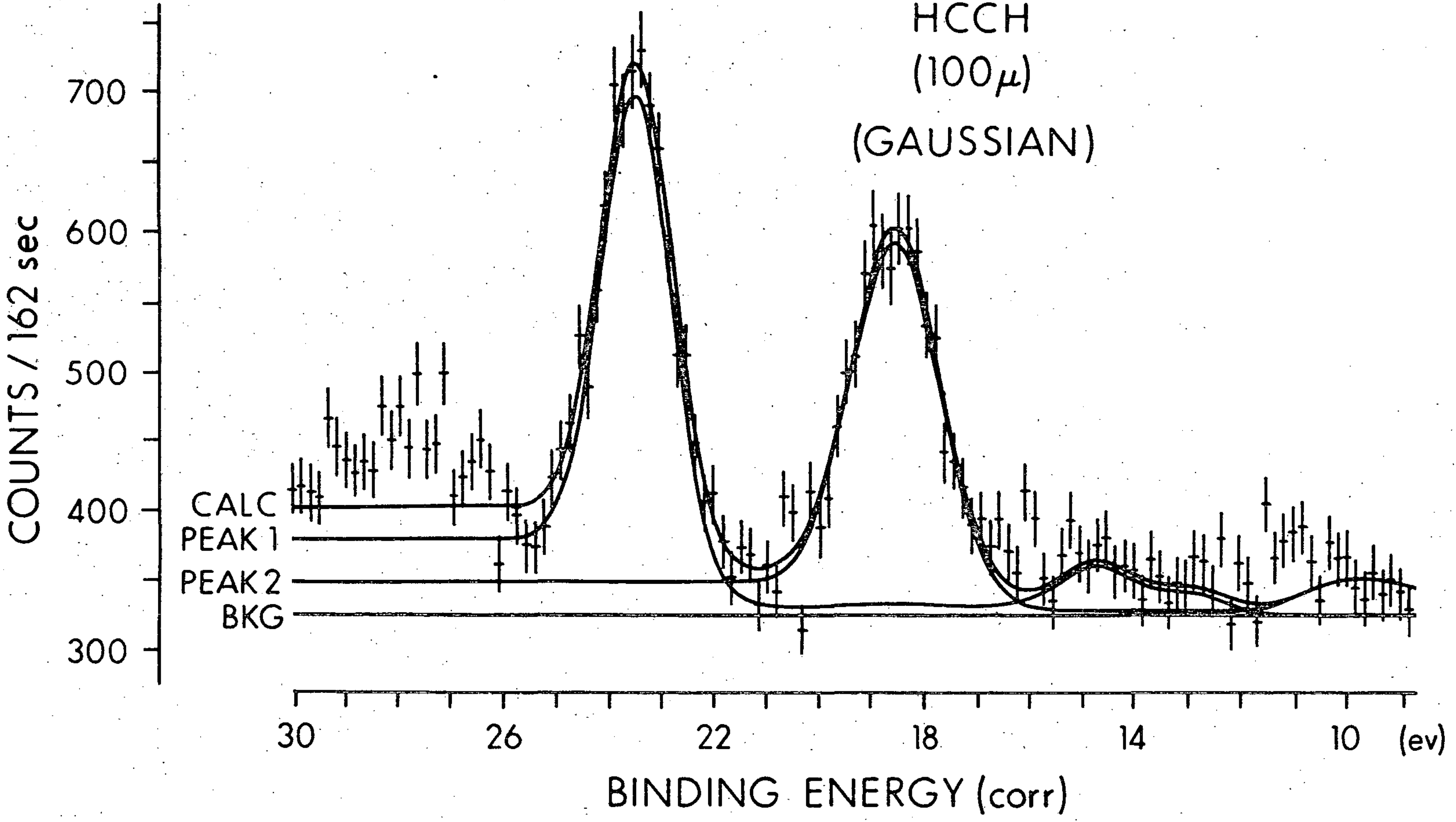

HCCH
(100μ)
(GAUSSIAN)
COUNTS / 162 sec
700
600
500
400
300
CALC
PEAK 1
PEAK 2
BKG
30
26
22
18
14
10
(ev)
BINDING ENERGY (corr)

Fig. 3.

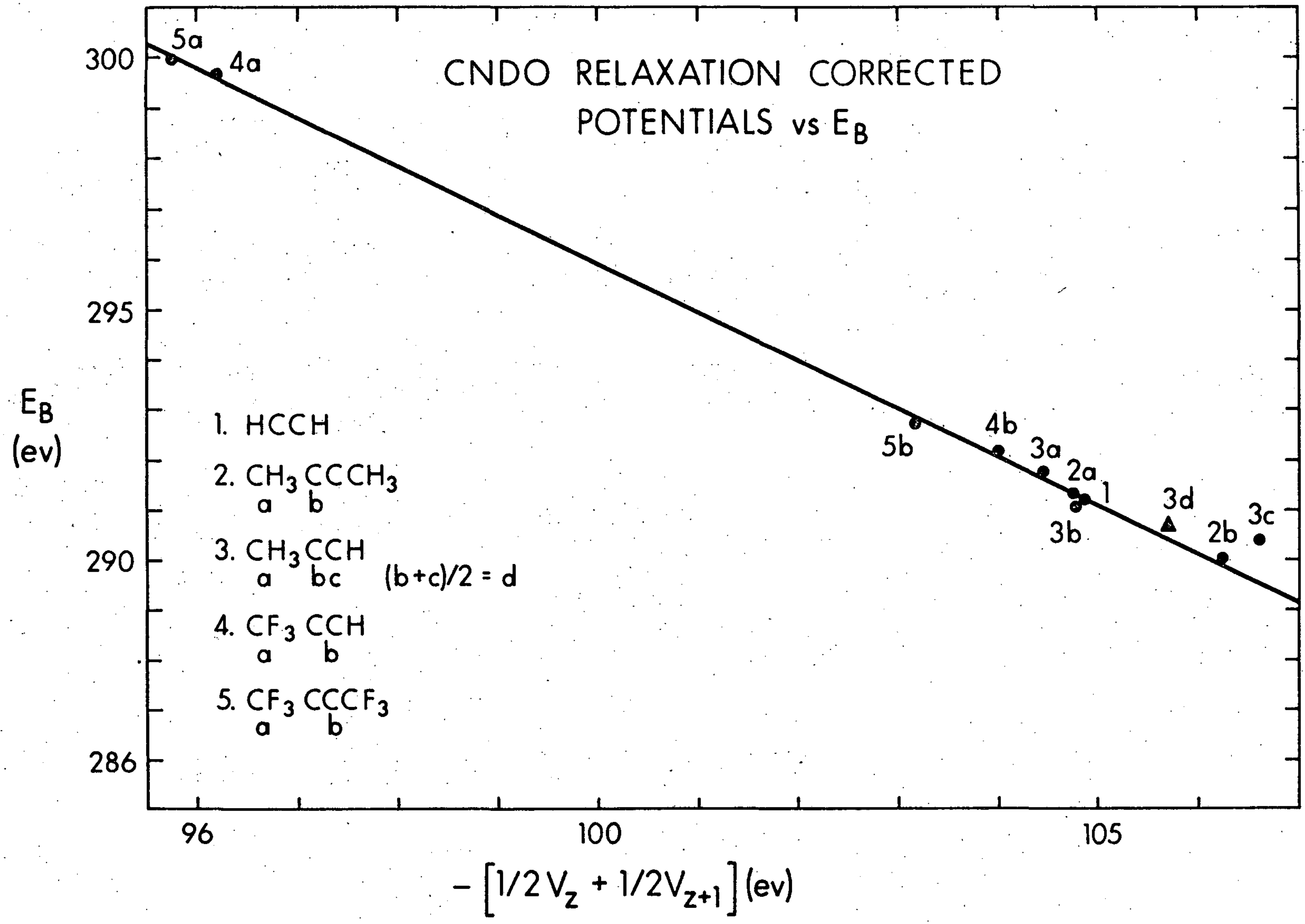

CNDO RELAXATION CORRECTED
POTENTIALS vs E_B
E_B (ev)
300
295
290
286
96
100
105
$-[1/2 V_Z + 1/2 V_{Z+1}]$ (ev)
5a
4a
5b
4b
3a
2a
1
3b
3d
2b
3c
1. HCCH
2. CH_3CCCH_3 a b
3. CH_3CCH a bc (b+c)/2 = d
4. CF_3CCH a b
5. CF_3CCCF_3 a b

Fig. 4.

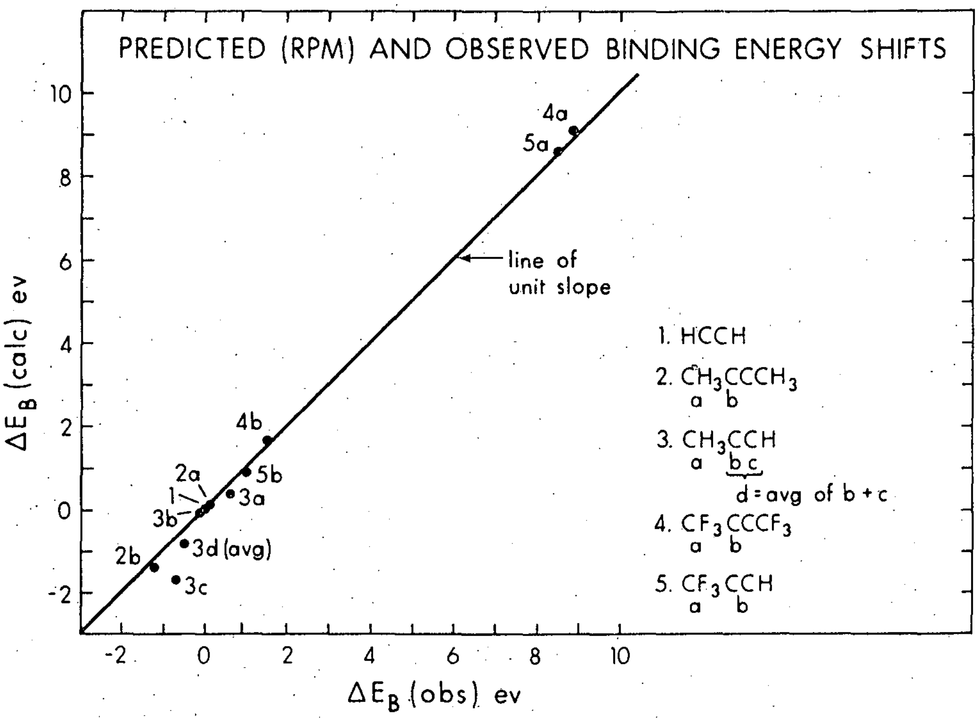

PREDICTED (RPM) AND OBSERVED BINDING ENERGY SHIFTS
ΔE_B (calc) ev
ΔE_B (obs) ev
-2
0
2
4
6
8
10
line of unit slope
4a
5a
4b
5b
2a
1
3b
3a
3d (avg)
2b
3c
1. HCCH
2. $\underset{a}{CH_3}\underset{b}{C}CCH_3$
3. $\underset{a}{CH_3}\underbrace{CCH}_{b\,c}$
d = avg of b + c
4. $\underset{a}{CF_3}\underset{b}{C}CCF_3$
5. $\underset{a}{CF_3}\underset{b}{C}CH$

Fig. 5

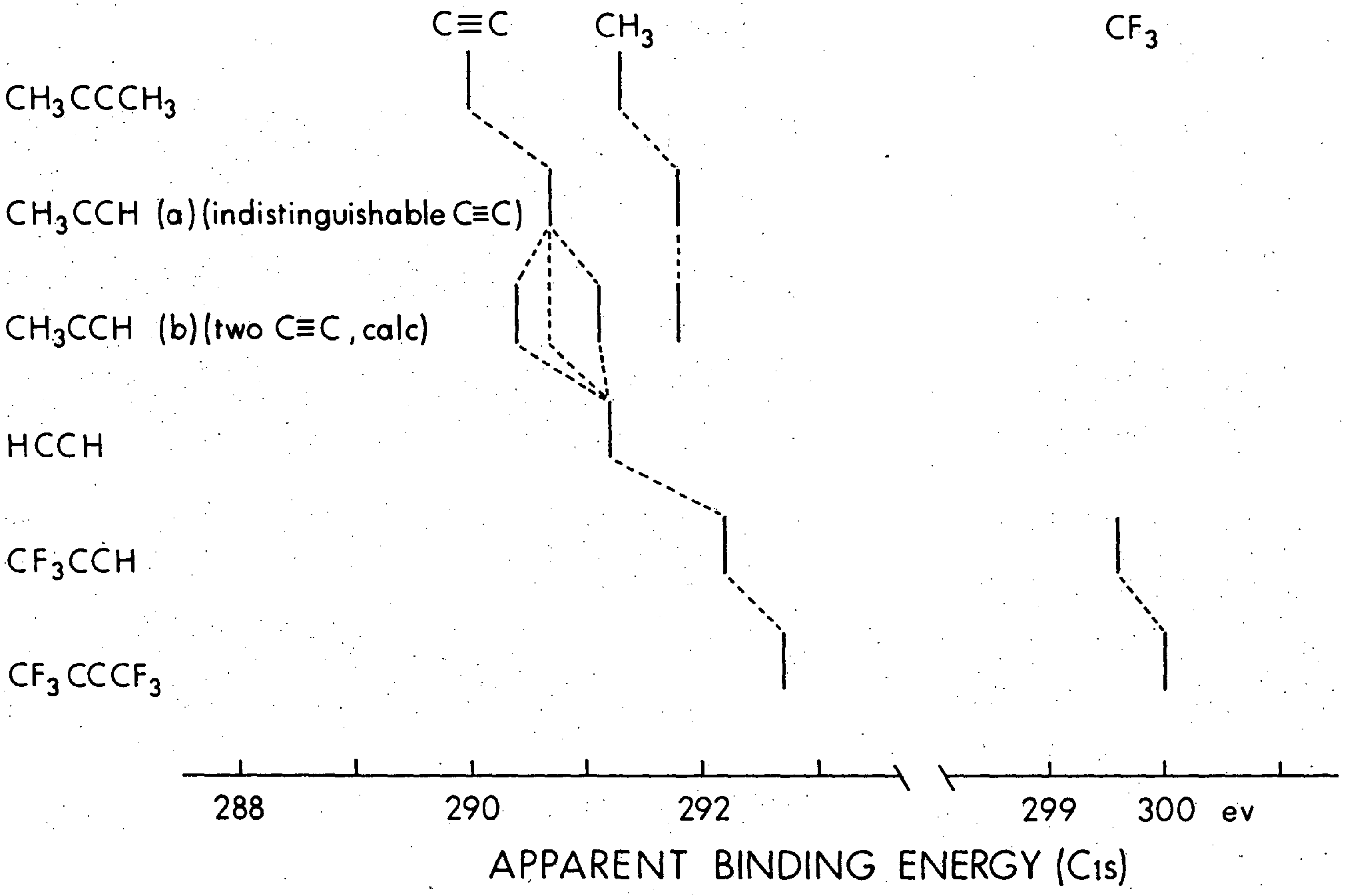

C≡C
CH3
CF3
CH3CCCH3
CH3CCH (a)(indistinguishable C≡C)
CH3CCH (b)(two C≡C, calc)
HCCH
CF3CCH
CF3CCCF3
288
290
292
299
300 ev
APPARENT BINDING ENERGY (C1s)

Fig. 6.

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