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CHARGE DISTRIBUTIONS IN MOLECULES AND IONS: MINDO 3 CALCULATIONS. AN ALTERNATIVE OF THE CHARGE LOCALISATION CONCEPT IN MASS SPECTROMETRY

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Abstract—The charge distributions in a series of molecules A and their ions A^+ and A^{2+} and in a second series B and their ions BH^+ and BH^{2+} are presented. It is shown that their distributions are consistent with the conventional concepts of electronegativity, but not with those of the intermediate ion structures in the charge localisation concept of fragmentation processes in mass spectrometry. The charge distributions show that the carbon adjacent to a heteroatom has a considerable positive charge which apparently makes its bond to the next carbon atom weak and prone to fission which is a dominant process in the fragmentation of the positive ion.

INTRODUCTION

It has been shown previously[1,2] that MINDO 3 calculations can successfully predict the pathway for the fragmentation or isomerisation of charged species. For such studies, MINDO 3 is a particularly appropriate semi-empirical quantum mechanical method since it is specifically adjusted to heats of formation data and moreover it adjusts the geometry of the species to produce the configuration of minimum localised energy.

While it is possible to calculate the reaction pathways for any molecule or ion, this requires a not inconsiderable computing time. Thus a more general approach is required and for the fragmentation processes in mass spectrometry the charge localisation concept has been widely used. In this approach the charge on the positive ion is to be put on the heteroatom. This clearly is in conflict with the conventional theories of organic reaction mechanisms in which the positive centre would never be located on the most electronegative atom. The present work is thus an investigation into the structures of ions and related molecules to examine the charge distribution in the ions, their geometry and heats of formation and to examine the charge localisation concept in the light of the results.

RESULTS

The results of the calculations are presented in two sections. In Table 1 the results of the series of species A, A^+ and A^{2+} are given while in Table 2 those of the species B, BH^+ and BH^{2+}. The two series of calculations were performed since the species A^+ and BH^{2+} had open shell configurations. Quantum mechanical calculations are usually less successful for such electronic configurations and a comparison of the two series would indicate any problems. A comparison of the results for the present calculations shows no significant discrepancy for the open shell species especially with respect to the charge distributions and it was thus established that useful comparisons could be made on the basis of the calculations.

The Tables include for each species, its charge, the enthalpy of formation of the gaseous species (kcal mol^{-1}), the ionisation energy (eV), the charge distribution in terms of the net charge on each atom and the difference in charge between the heteroatom (X) and the adjacent carbon atom (C_α), $\Delta q(C_\alpha–X)$. Where they are available the experimentally determined values of ΔH_f are given in brackets. As can be seen the agreement is very good. The detailed geometrically optimised structure of each species is given in the Appendix.

Charge distributions

It is clear from the results that there is a considerable difference in charge $\Delta q(C_\alpha–X)$ between the adjacent carbon atom and the heteroatom (X) in all the species listed. The charge on the carbon atom is always more positive than the heteroatom (F or O) which is negatively charged even in the dipositive ions. For species with single bonds between C_α and X, and with one heteroatom, $\Delta q(C_\alpha–X)$ increases somewhat as the positive charge increases from zero to two, the α-carbon atom becoming more positive with respect to the heteroatom. The sixth column of the tables shows this tendency. When the heteroatom is nitrogen, it can have a positive charge but this is always less than that of the neighbouring carbon atom.

When the heteroatom is doubly bonded to the carbon atom the polarity of the bond is decreased in going from A to A^+ but increases again from A^+ to A^{2+}.

For heterocyclic compounds for which calculations have been performed, furan and pyrrole, there is a greater increase in $\Delta q(C_\alpha–X)$ as the number of positive charges on the species increases. Again the polarity is greater with X = oxygen or halogen and somewhat less for X = nitrogen.

In all the compounds calculated to date, the C–X bond can be best represented by the symbol $-\overset{\delta+}{C}-\overset{\delta-}{X}$ and on the symbology used in the charge localisation concept this would correspond to $-\overset{+}{C}{}^{\cdot}-X$ and not $-C-\overset{+}{X}{}^{\cdot}$. This conclusion is supported by the X-ray photoelectron spectroscopy studies and CNDO/2 calculations of Davies *et al.*[3] for difluorobenzene in the ground state and by similar work of Ohta *et al.*[4] for hydroquinone.

It is clear that the charge distributions are dominated by the conventional ideas of electronegativity and hence

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Table 1.

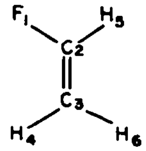
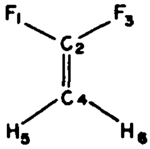
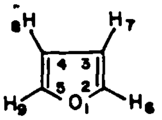
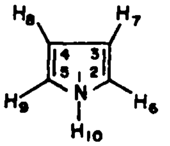
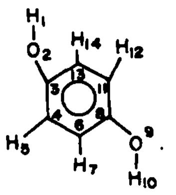
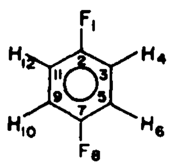
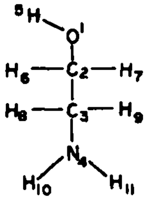
Structure	Charge distributions	
	A	F_1, −0.3279; C_2, 0.4711; C_3, −0.2315; H_4, 0.0708; H_5, −0.0366; H_6, 0.0541 (ΔH_f = −29.5 (−28.0); I.P = 10.03 (10.3); $\Delta q(C_\alpha - X)$ = 0.80)
	A^+	F_1, −0.1536; C_2, 0.6493; C_3, 0.1178; H_4, 0.1527; H_5, 0.0949; H_6, 0.1390 (ΔH_f = 189.1; I.P. = 13.3; $\Delta q(C_\alpha - X)$ = 0.79)
	A^{2+}	F_1, −0.0063; C_2, 0.8710; C_3, 0.3527; H_4, 0.2554; H_5, 0.2719; H_6, 0.2553 (ΔH_f = 563.3; I.P. = 27.0; $\Delta q(C_\alpha - X)$ = 0.88)
	A	F_1, −0.3520; C_2, 0.9259; F_3, −0.3519; C_4, −0.4365; H_5, 0.1734; H_6, 0.1072 (ΔH_f = −86.1 (−80.5); I.P. = 10.2; $\Delta q(C_\alpha - X)$ = 0.73)
	A^+	F_1, −0.2042; C_2, 1.0626; F_3, −0.2040; C_4, −0.0011; H_5, 0.1734; H_6, 0.1733 (ΔH_f = 136.8; I.P. = 13.6; $\Delta q(C_\alpha - X)$ = 0.79)
	A^{2+}	F_1, −0.0505; C_2, 1.1315; F_3, −0.0489; C_4, 0.4975; H_5, 0.2353; H_6, 0.2350 (ΔH_f = 542.3; I.P. = 26.6; $\Delta q(C_\alpha - X)$ = 0.83)
	A	O_1, −0.3111; C_2, 0.2288; C_3, −0.1083; C_4, −0.1082; C_5, 0.2288; H_6, 0.0082; H_7, 0.0268; H_8, 0.0268; H_9, 0.0082 (ΔH_f = −8.03 (−8.3); I.P. = 8.4; $\Delta q(C_\alpha - X)$ = 0.54)
	A^+	O_1, −0.2769; C_2, 0.4528; C_3, −0.0368; C_4, −0.0362; C_5, 0.4532; H_6, 0.1000; H_7, 0.1221; H_8, 0.1218; H_9, 0.1001 (ΔH_f = 173.0; I.P. = 11.2; $\Delta q(C_\alpha - X)$ = 0.73)
	A^{2+}	O_1, −0.2880; C_2, 0.7332; C_3, 0.0050; C_4, 0.0077; C_5, 0.7329; H_6, 0.1875; H_7, 0.2170; H_8, 0.2170; H_9, 0.1876 (ΔH_f = 508.8; I.P. = 22.8; $\Delta q(C_\alpha - X)$ = 1.02)
	A	N_1, 0.0808; C_2, −0.0283; C_3, −0.0655; C_4, −0.0615; C_5, −0.0320; H_6, 0.0204; H_7, 0.0155; H_8, 0.0126; H_9, 0.0226; H_{10}, 0.0355 (ΔH_f = 29.2 (24.6); I.P. = 8.2(8.20); $\Delta q(C_\alpha - N)$ = −0.11)
	A^+	N_1, 0.0488; C_2, 0.2104; C_3, −0.0088; C_4, −0.0079; C_5, 0.2090; H_6, 0.0968; H_7, 0.1110; H_8, 0.1070; H_9, 0.0991; H_{10}, 0.1346 (ΔH_f = 205; I.P. = 11.0; $\Delta q(C_\alpha - N)$ = 0.16)
	A^{2+}	N_1, −0.0026; C_2, 0.5159; C_3, −0.0698; C_4, 0.1667; C_5, 0.4061; H_6, 0.1663; H_7, 0.2159; H_8, 0.1864; H_9, 0.1874; H_{10}, 0.2278 (ΔH_f = 536.2; I.P. = 21.9; $\Delta q(C_\alpha - N)$ = 0.52)
	A	H_1, 0.2423; O_2, −0.4419; C_3, 0.3155; C_4, −0.0647; H_5, 0.0228; C_6, −0.1095; H_7, 0.0157; C_8, 0.3177; O_9, −0.4401; H_{10}, 0.2440; C_{11}, −0.0390; H_{12}, 0.0129; C_{13}, −0.0937; H_{14}, 0.0180. (ΔH_f = −82.2(−70.8); I.P. = 7.9 eV; $\Delta q(C_\alpha - O)$ = 0.76)
	A^+	H_1, 0.3017; O_2, −0.3406; C_3, 0.4723; C_4, −0.0211; H_5, 0.0879; C_6, −0.0833; H_7, 0.0840; C_8, 0.4726; O_9, −0.3423; H_{10}, 0.3014; C_{11}, −0.0201; H_{12}, 0.0911; C_{13}, −0.0836; H_{14}, 0.0801. (ΔH_f = 85.0; I.P. = 9.9; $\Delta q(C_\alpha - O)$ = 0.81)
	A^{2+}	H_1, 0.3546; O_2, −0.2125; C_3, 0.5872; C_4, 0.0355; H_5, 0.1546; C_6, −0.0749; H_7, 0.1556; C_8, 0.6251; O_9, −0.2313; H_{10}, 0.3487; C_{11}, −0.0215; H_{12}, 0.1560; C_{13}, −0.0284; H_{14}, 0.1514 (ΔH_f = 381.9; I.P. = 20.4; $\Delta q(C_\alpha - O)$ = 0.80)
	A	F_1, −0.3335; C_2, 0.3966; C_3, −0.0769; H_4, 0.0466; C_5, −0.0761; H_6, 0.0426; C_7, 0.3942; F_8, −0.3304; C_9, −0.0753; H_{10}, 0.0444; C_{11}, −0.0769; H_{12}, 0.0448 (ΔH_f = −69.1 (−73.3); I.P. = 8.9 (9.15); $\Delta q(C_\alpha - F)$ = 0.73)
	A^+	F_1, −0.2157; C_2, 0.5698; C_3, −0.0488; H_4, 0.1233; C_5, −0.0485; H_6, 0.1163; C_7, 0.5666; F_8, −0.2046; C_9, −0.0534; H_{10}, 0.1161; C_{11}, −0.0442; H_{12}, 0.1232 (ΔH_f = 125.0; I.P. = 11.2(9.15); $\Delta q(C_\alpha - F)$ = 0.79)
	A^{2+}	F_1, −0.0863; C_2, 0.7398; C_3, −0.0195; H_4, 0.1899; C_5, −0.0278; H_6, 0.1937; C_7, 0.7517; F_8, −0.0829; C_9, −0.0288; H_{10}, 0.1884; C_{11}, −0.0120; H_{12}, 0.1937 (ΔH_f = 449.3; I.P. = 21.4; $\Delta q(C_\alpha - F)$ = 0.83)
	A	O_1, −0.1248; C_2, −0.0317; C_3, 0.02049; N_4, −0.1924; H_5, 0.1137; H_6, 0.1712; H_7, −0.0917; H_8, −0.0744; H_9, −0.0810; H_{10}, 0.0552; H_{11}, 0.0509 (ΔH_f = −8.7; I.P. = 7.7; $\Delta q(C-O)$ = 0.091; $\Delta q(C-N)$ = 0.40)
	A^+	O_1, −0.1690; C_2, 0.2377; C_3, 0.1287; N_4, −0.0831; H_5, 0.280; H_6, 0.2847; H_7, 0.0011; H_8, 0.0383; H_9, 0.0545; H_{10}, 0.1114; H_{11}, 0.1151 (ΔH_f = 150.4; I.P. = 10.1; $\Delta q(C-O)$ = 0.41; $\Delta q(C-N)$ = 0.21 Geometry change)

Table 1. (*Cont.*).

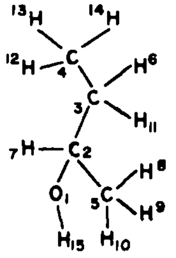
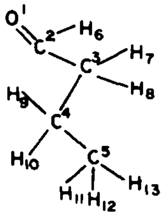
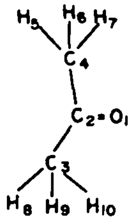
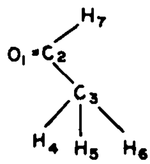
Structure	Charge distributions	
	A^{2+}	O_1, −0.2654; C_2, 0.3691; C_3, 0.0766; N_4, 0.1162; H_5, 0.4143; H_6, 0.4073; H_7, 0.1367; H_8, 0.1605; H_9, 0.1705; H_{10}, 0.2051; H_{11}, 0.2091 (ΔH_f = 424.0; I.P. = 10.1; Δq(C–O) = 0.64; Δq(C–N) = 0.04)
	A	O_1, −0.4831; C_2, 0.4112; C_3, 0.0067; C_4, 0.0793; C_5, 0.0194; H_6, −0.0269; H_7, −0.1234; H_8, 0.0026; H_9, −0.0211; H_{10}, −0.008; H_{11}, −0.0243; H_{12}, −0.0209; H_{13}, −0.0266; H_{14}, −0.0291; H_{15}, 0.2442 (ΔH_f = −74.3; I.P. = 10.4; Δq(C–O) = 0.89)
	A^+	O_1, −0.2188; C_2, 0.1896; C_3, 0.071; C_4, 0.0411; C_5, 0.0031; H_6, 0.092; H_7, 0.3352; H_8, 0.0458; H_9, 0.0421; H_{10}, 0.0674; H_{11}, 0.0349; H_{12}, 0.0433; H_{13}, 0.008; H_{14}, 0.0061; H_{15}, 0.3022 (ΔH_f = 120.5; I.P. = 9.4; Δq(C–O) = 0.41)
	A^{2+}	O_1, −0.2706; C_2, 0.6819; C_3, −0.0669; C_4, 0.037; C_5, −0.1559; H_6, 0.1373; H_7, 0.4012; H_8, 0.1806; H_9, 0.1439; H_{10}, 0.1808; H_{11}, 0.1183; H_{12}, 0.1128; H_{13}, 0.0413; H_{14}, 0.0554; H_{15}, 0.4028 (ΔH_f = 412.9; I.P. = 21.4; Δq(C–O) = 0.95)
	A	O_1, −0.4663; C_2, 0.6051; C_3, −0.0389; C_4, 0.1063; C_5, 0.0609; H_6, −0.1371; H_7, −0.0112; H_8, 0.0038; H_9, −0.0399; H_{10}, −0.0273; H_{11}, −0.0259; H_{12}, −0.0110; H_{13}, −0.0184 (ΔH_f = −55.9(−53.7); I.P. = 10.1(9.86); $\Delta q(C_\alpha{=}O)$ = 1.07)
	A^+	O_1, −0.2176; C_2, 0.5859; C_3, −0.0151; C_4, 0.0801; C_5, 0.0362; H_6, 0.2980; H_7, 0.0762; H_8, 0.0691; H_9, 0.0244; H_{10}, 0.0181; H_{11}, −0.0246; H_{12}, 0.0287; H_{13}, 0.0406 (ΔH_f = 137.3; I.P. = 10.7; $\Delta q(C_\alpha{=}O)$ = 0.80. Geometry Change)
	A^{2+}	O_1, −0.1638; C_2, 0.9476; C_3, −0.0385; C_4, 0.1122; C_5, −0.008, H_6, 0.4775; H_7, 0.1671; H_8, 0.1675; H_9, 0.0930; H_{10}, 0.0416; H_{11}, 0.0447; H_{12}, 0.0413; H_{13}, 0.1179 (ΔH_f = 448.8; I.P. = 20.6; $\Delta q(C_\alpha{=}O)$ = 1.11 Geometry Change)
	A	O_1, −0.5015; C_2, 0.5660; C_3, −0.0664; C_4, −0.0667; H_5, 0.0230; H_6, 0.0230; H_7, −0.0120; H_8, 0.0242; H_9, 0.0212; H_{10}, −0.0112 (ΔH_f = −52.9(−51.9); I.P. = 9.91; $\Delta q(C_\alpha{=}O)$ = 1.07)
	A^+	O_1, −0.1908; C_2, 0.6294; C_3, −0.0083; C_4, −0.0092; H_5, 0.1097; H_6, 0.1117; H_7, 0.0682; H_8, 0.1124; H_9, 0.1074; H_{10}, 0.0695 (ΔH_f = 164.7; I.P. = 12.9; $\Delta q(C_\alpha{=}O)$ = 0.82)
	A^{2+}	O_1, −0.0319; C_2, 0.8374; C_3, −0.0515; C_4, −0.0523; H_5, 0.2032; H_6, 0.2023; H_7, 0.2444; H_8, 0.2089; H_9, 0.1981; H_{10}, 0.2414 (ΔH_f = 526.3; I.P. = 24.0; $\Delta q(C_\alpha{=}O)$ = 0.87)
	A	O_1, −0.4634; C_2, 0.6170; C_3, −0.0680; H_4, 0.0217; H_5, 0.0208; H_6, 0.0134; H_7, −0.1416 (ΔH_f = −43.8(−39.7); I.P. = 10.3(10.28); $\Delta q(C_\alpha{=}O)$ = 1.08)
	A^+	O_1, −0.1088; C_2, 0.6379; C_3, −0.0431; H_4, 0.1305; H_5, 0.1216; H_6, 0.1067; H_7, 0.1553. (ΔH_f = 184.0; I.P. = 13.7; $\Delta q(C_\alpha{=}O)$ = 0.75 Geometry Change)
	A^{2+}	O_1, −0.1402; C_2, 1.0304; C_3, −0.1242; H_4, 0.2426; H_5, 0.2427; H_6, 0.2425; H_7, 0.5068 (ΔH_f = 484.5; I.P. = 26.2; $\Delta q(C_\alpha{=}O)$ = 1.17)

Table 2.

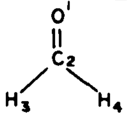
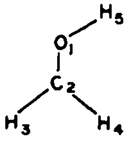
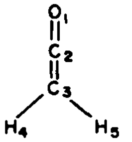
Structure	Charge distributions	
	B	O_1, −0.425; C_2, 0.6432; H_3, −0.1091; H_4, −0.1091 (ΔH_f = −25.6(−25.9); I.P. = 10.7(10.87); Δq(C=O) = 1.07
	BH^+	O_1, −0.2144; C_2, 0.6836; H_3, 0.1118; H_4, 0.0579; H_5, 0.3611 (ΔH_f = 156.8; I.P. = 19.6; Δq(C=O) = 0.90)
	BH^{2+}	O_1, −0.0154; C_2, 0.8021; H_3, 0.3478; H_4, 0.3467; H_5, 0.5188 (ΔH_f = 588.7; I.P. = 22.3; Δq(C=O) = 0.82)
	B	O_1, −0.4167; C_2, 0.6725; C_3, −0.4728; H_4, 0.1085; H_5, 0.1085 (ΔH_f = −20.7(−14.2); I.P. = 9.2; Δq(C=O) = 1.09)

Table 2. (*Cont.*).

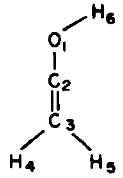
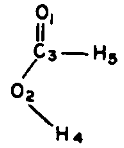
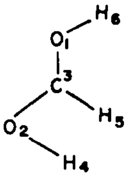
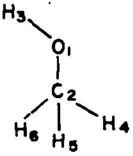
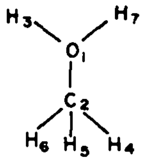
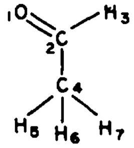
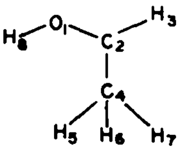
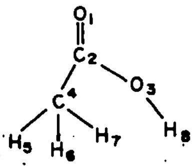
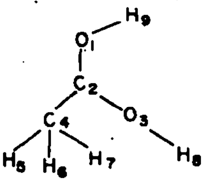
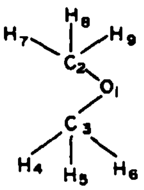
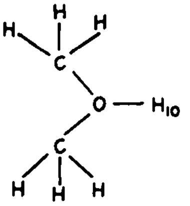
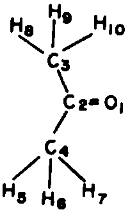
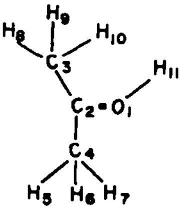
Structure	Charge distribution	
	BH^+	O_1, −0.2100; C_2, 0.6428; C_3, −0.1848; H_4, 0.1997; H_5, 0.1996; H_6, 0.3526; (ΔH_f = 160.1; I.P. = 17.0; $\Delta q(C{=}O)$ = 0.85)
	BH^{2+}	O_1, −0.1000; C_2, 0.8968; C_3, 0.1600; H_4, 0.2684; H_5, 0.2674; H_6, 0.5074; (ΔH_f = 530.7; I.P. = 19.6; $\Delta q(C{=}O)$ = 1.00)
	B	O_1, −0.5412; O_2, −0.4992; C_3, 0.8564; H_4, 0.2699; H_5, −0.0859 (ΔH_f = 88.8 (−90.6); I.P. = 11.2(11.1); $\Delta q(C_3{=}O_1)$ = 1.40; $\Delta q(C_3{=}O_2)$ = 1.36)
	BH^+	O_1, −0.3739; O_2, −0.3223; C_3, 0.9099; H_4, 0.3585; H_5, 0.0634; H_6, 0.3645 (ΔH_f = 85.1; I.P. = 19.5; $\Delta q(C_3{=}O_1)$ = 1.28; $\Delta q(C_3{-}O_2)$ = 1.23)
	BH^{2+}	O_1, −0.1561; O_2, −0.1820; C_3, 1.0199; H_4, 0.4832; H_5, 0.3473; H_6, 0.4877 (ΔH_f = 514.2; I.P. = 22.0; $\Delta q(C_3{=}O_1)$ = 1.18; $\Delta q(C_3{-}O_2)$ = 1.20)
	B	O_1, −0.4457; C_2, −0.4309; H_3, 0.2490; H_4, −0.0959; H_6, −0.0449 (ΔH_f = −50.6 (−48.1); I.P. = 11.1(10.9); $\Delta q(C_\alpha{-}O)$ = 0.88)
	BH^+	O_1, −0.2168; C_2, 0.3181; H_3, 0.3605; H_4, 0.0466; H_5, 0.0747; H_6, 0.0563; H_7, 0.3603 (ΔH_f = 137.2; I.P. = 19.0; $\Delta q(C_\alpha{-}O)$ = 0.54)
	BH^{2+}	O_1, −0.1534; C_2, 0.4554; H_3, 0.4617; H_4, 0.2321; H_5, 0.2798; H_6, 0.2767; H_7, 0.4477 (ΔH_f = 545.9; I.P. = 20.4; $\Delta q(C_\alpha{-}O)$ = 0.61)
	B	O_1, −0.4634; C_2, 0.6170; H_3, −0.1416; C_4, −0.0680; H_5, 0.2170; H_6, 0.0208; H_7, 0.0134 (ΔH_f = −43.8(−39.7); I.P. = 10.3(10.28); $\Delta q(C{=}O)$ = 1.08)
	BH^+	O_1, −0.2722; C_2, 0.6702; H_3, 0.0615; C_4, −0.1320; H_5, 0.0988; H_6, 0.1248; H_7, 0.1129; H_8, 0.336 ΔH_f = − 124.6; I.P. = 18.3; $\Delta q(C{=}O)$ = 0.94)
	BH^{2+}	O_1, −0.1471; C_2, 0.6667; H_3, 0.2006; C_4, 0.0006; H_5, 0.3366; H_6, 0.2403; H_7, 0.2958; H_8, 0.4064 (ΔH_f = 529.8; I.P. = 19.9; $\Delta q(C{=}O)$ = 0.81)
	B	O_1, −0.5330; C_2, 0.8305; O_3, −0.5119; C_4, −0.1124; H_5, 0.0357; H_6, 0.0247; H_7, 0.0089; H_8, 0.2575 (ΔH_f = −101.7(−103.3); I.P. = 10.7(10.35); $\Delta q(C_2{=}O_1)$ = 1.36; $\Delta q(C_2{-}O_3)$ = 1.34)
	BH^+	O_1, −0.3703; C_2, 0.9066; O_3, −0.4179; C_4, −0.1338; H_5, 0.1162; H_6, 0.1103; H_7, 0.0941; H_8, 0.3465; H_9, 0.3483 (ΔH_f = 55.7; I.P. = 18.4; $\Delta q(C_2{=}O_1)$ = 1.28; $\Delta q(C_2O_3)$ = 1.32)
	BH^{2+}	O_1, −0.2684; C_2, 1.0092; O_3, −0.3026; C_4, −0.0043; H_5, 0.2238; H_6, 0.2312; H_7, 0.2197; H_8, 0.4527; H_9, 0.4388 (ΔH_f = 457.7; I.P. = 20.0; $\Delta q(C_2{=}O_1)$ = 1.28; $\Delta q(C_2{-}O_3)$ = 1.31)
	B	O_1, −0.4057; C_2, 0.4293; C_3, 0.4292; H_4, −0.0473; H_5, −0.0901; H_6, −0.0889; H_7, −0.0892; H_8, −0.0472; H_9, −0.0901 (ΔH_f = −42.7(−44.0); I.P. = 10.5(10.0); $\Delta q(C{-}O)$ = 0.84)
	BH^+	O_1, −0.1967; C_2, 0.2661; C_3, 0.3250; H_4, 0.0950; H_5, −0.0354; H_6, 0.1039; H_7, 0.0416; H_8, 0.0282; H_9, 0.0472; H_{10}, 0.3252 (ΔH_f = 190.6; I.P. = 15.8; $\Delta q(C{-}O)$ = 0.52)

Table 2. (*Cont.*).

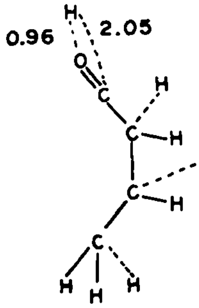
Structure	Charge distribution	
	BH^{2+}	O_1, −0.2189; C_2, 0.2999; C_3, 0.4977; H_4, 0.2739; H_5, 0.2053; H_6, 0.2060; H_7, 0.1227; H_8, 0.1017; H_9, 0.0881; H_{10}, 0.4236 (ΔH_f = 534.1; I.P. = 18.5; Δq(C–O) = 0.72)
	B	O_1, −0.5015; C_2, 0.5660; C_3, −0.0664; C_4, −0.0667; H_5, 0.0230; H_6, 0.0230; H_7, −0.0120; H_8, 0.0242; H_9, 0.0212; H_{10}, −0.0112 (ΔH_f = −52.9(−51.9); I.P. = 9.9(9.92); Δq(C=O) = 1.07)
	BH^+	O_1, −0.3304; C_2, 0.6646; C_3, −0.0958; C_4, −0.1356; H_5, 0.1006; H_6, 0.1015; H_7, 0.0837; H_8, 0.1054; H_9, 0.1069; H_{10}, 0.0746; H_{11}, 0.3244 (ΔH_f = 103.2; I.P. = 17.4; Δq(C=O) = 0.99)
	BH^{2+}	O_1, −0.2521; C_2, 0.8034; C_3, −0.0357; C_4, −0.0250; H_5, 0.1813; H_6, 0.1819; H_7, 0.1510; H_8, 0.1945; H_9, 0.1887; H_{10}, 0.1518; H_{11}, 0.4602 (ΔH_f = 484.6; I.P. = 19.2; Δq(C=O) = 1.06)

by the effective nuclear charge of the atoms of the species. This is consistent with the theory of organic reaction mechanisms but is not consistent with the charge localisation concept of mass spectrometry.

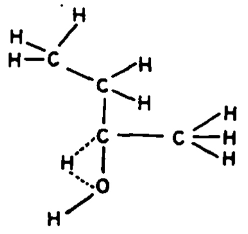
Oxygen containing species

In many of the species where oxygen is the heteroatom it will be noticed from the tables that the charge distribution on the A^+ and BH^+ species show some differences from the correlations discussed above. For the protonated species B, BH^+ and BH^{2+} the α-carbon atom is always more positive than the heteroatom. However, on protonation of the heteroatom (oxygen) in forming BH^+ from B, there is a reduction in the polarity of the C–X bond.

This is accompanied by a large degree of positive charge remaining on the proton which is attached to the heteroatom, giving a charge distribution which can be represented by $-\overset{\delta+}{C}-\overset{\delta-}{O}-\overset{\delta+}{H}$. This is a particularly stable arrangement and this conclusion from the present work is supported by that of Hopkinson and Csizmadia[5] using *ab initio* calculations, and by Ohkubo *et al.*[6] who used INDO calculations. Again the governing principle is the effective nuclear charge of the competing atom. The stability of the arrangement is evident in the calculations of a number of the A^+ and A^{2+} species involving oxygen. In *n*-butanal and butan-2-ol the preferred geometrical arrangements for the A^+ and A^{2+} species are ones in which a hydrogen atom has been transferred to the oxygen heteroatom.



Butanal A^+ and A^{2+}



Butan–2–ol, A^+ and A^{2+}

The transfer of the H atom occurs with no intervening localised minima and occurs during the application of the geometrical adjustment minimisation procedure of the MINDO 3 calculations.

It is remarkable how much of the positive charge can be carried by the hydrogen atoms in the species. The result of protonation of the heteroatom (forming BH^+) or the transfer of hydrogen atom to the oxygen atom in the A^+ species is a decrease in the polarity of the C–X bond, with the hydrogen atom carrying a significant positive charge of between (1/4) and (1/2).

Fragmentation processes in mass spectrometry

The high charge on many of the hydrogen atoms in the ions, especially on groups such as C–O–H would indicate H^+ elimination would occur in fragmentation processes. Such eliminations are not prevalent in mass spectral processes and the reason in undoubtedly due to the large ΔH_f of H^+ compared with the larger alkyl ions. The ΔH_f values are compared in Table 3.

The ΔH_f of these ions is so much higher than those of the radicals likely to be involved in mass spectral processes, that the ΔH_f of the ions tend to dominate the energetics of the fragmentation processes.

In the charge localisation concept no account is taken of energetics of the fragmentation processes and indeed it would be difficult to calculate the enthalpies of formation of larger species. Thus this alternative approach is often required and is most useful. It is supposed that the electron on ionisation is removed from the heteroatom since the heteroatom will contain lone pairs of electrons which are presumably easier to ionise than bonded elec-

Table 3.

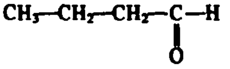
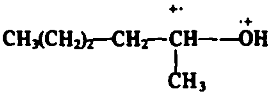
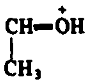
Ion	H^+	CH_3^+	$C_2\overset{+}{H}_5$	$(CH_3)_3C^+$	$(CH_3)_2\overset{+}{C}H$	$C_3H_5^+$	$CH_2O\overset{+}{H}$
ΔH_f (kcal mol^{-1})	366	260	219	176	290	226	169

Table 4. ΔH_f of free radicals

Radical	H	CH_3	C_2H_5	$(CH_3)_3C$	$(CH_3)_2CH$	C_3H_5	CH_2OH	CH_3O
ΔH_f (kcal mol^{-1})	52.1	34.0	25	4.5	16.8	40.0	−6	3.5

trons. This is of course not always true as in one of the lone pairs of electrons on formaldehyde (methanal) which is mainly 2s in character. However, while this may be the initial process, there is no necessity for this electronic arrangement to have any significant lifetime. Electron re-arrangements can occur in about 10^{-16} s which are over 10^3 times faster than any atom re-arrangement processes (e.g. fragmentations). Despite the contradiction in terms of electronegativities, intermediates with the positive charge on the heteroatom ($-C-\overset{+}{X}^{\cdot}$) are shown as intermediates in the mechanisms based on the charge localisation concept which immediately precede fragmentation. Examples are shown in Table 5.

Table 5. Intermediates in conventional charge localisation mechanisms

Molecular ion	Fragment ion	*m/e* value
 $CH_3-CH_2-CH_2-\underset{\overset{\|}{O}}{C}-H$	$\overset{+}{O}\equiv C-H$	29
 $CH_3(CH_2)_2-CH_2-\overset{+\cdot}{\underset{CH_3}{CH}}-\overset{\cdot+}{O}H$	 $\underset{CH_3}{CH}=\overset{+}{O}H$	45

It has been shown earlier that the most energetically stable configuration for a positively charged ion is not that with the positive charge on the heteroatom but with it on the carbon atom adjacent to the heteroatom. Thus on the grounds of simple electronegativity arguments and shown clearly by the present calculations the latter species would be formed rapidly. The configuration present can be represented as $-C-\overset{+}{C}-\overset{-}{X}$. The dominant feature of the bulk of fragmentation processes is the cleavage of the β-bond. This is explained very simply on the basis of the correct intermediate. The charge on the α-carbon atom has effectively weakened the β-C–C bond which becomes the weakest bond in the ion.

Preferential cleavage of this bond occurs with the positive charge remaining on the fragment containing the α-carbon atom.

The polarity of the C–X bond depends on the nature of X and increases in the order halogen (F) > O > N. In the first of these the C–X bond may be weak enough to break but usually the $-C_\beta-C_\alpha(-X)$ is dissociated preferentially on fragmentation. The competing effects of O and N are shown in the calculations on 2-aminoethanol where the bond β to the oxygen atom is the weakest.

In the case of oxygen containing compounds such as butanal and aliphatic alcohols the calculations show the most favourable configuration is where a H-atom has been transferred to the oxygen atom. This is precisely what occurs in the McLafferty-type re-arrangements. Before the calculations were performed it was thought possible that the H-atom which could form the 6-membered ring with the oxygen atom in the McLafferty formulation would, as with other H atoms in these molecules, carry a significant positive charge. This has proved to be incorrect and the best configuration of the positive ion is where an H-atom is transferred to the oxygen atom. When this occurs in alcohols this can lead to the ready elimination of water which characterises the mass spectra of aliphatic alcohols.

To summarise it is proposed that the charge localisation concept should be modified as follows:

1. In the ion the positive charge should be placed on the α-carbon atom.
2. The β-bond is thereby the weakest in the ion and cleaves.
3. H-atoms can carry a significant positive charge but do not dissociate due to unfavourable energetics.
4. Hydrogen atom transfer occurs to oxygen atoms resulting in McLafferty re-arrangements in aldehydes and ketones, and elimination of water in alcohols.

The above calculations support in general terms the comments of Williams and Beynon[7] as to the general usefulness of the charge localisation concept but show that the conventional representations of charges in ions need revision and the true representations are more consistent with a molecular orbital concept since the charges vary throughout the molecules and ions.

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[7] D. H. Williams and J. H. Beynon, *Org. Mass Spec.* 11, 103 (1976).

APPENDIX

Details of bond lengths (Å) and angles for the geometrically optimised structures. The numbering of the atoms is given in Tables 1 and 2.

Fluoroethylene (*A*). C_2-F_1, 1.365; C_2-C_3, 1.310; C_3-H_4, 1.094;

$C_3{-}H_6$, 1.097; $C_2{-}H_5$, 1.098; $C_3C_2F_1$, 123.3; $C_2C_3H_4$, 125.1; $C_2C_3H_6$, 121.8; $C_3C_2H_5$, 131.3.

A^+ $C_2{-}F_1$, 1.301; $C_2{-}C_3$, 1.379; $C_3{-}H_4$, 1.099; $C_3{-}H_6$, 1.093; $C_2{-}H_5$, 1.098; $C_3C_2F_1$, 108.1; $C_2C_3H_4$, 122.3; $C_2C_3H_6$, 123.5; $C_3C_2H_5$, 137.9.

A^{2+} $C_2{-}F_1$, 1.366; $C_2{-}C_3$, 1.410; $C_3{-}H_4$, 1.117; $C_3{-}H_6$, 1.109; $C_2{-}H_5$, 1.117; $C_3C_2F_1$, 70.2; $C_2C_3H_4$, 122.2; $C_2C_3H_6$, 122.1; $C_3C_2H_5$, 169.3.

Difluoroethylene (*A*). $C_2{-}F_1$, 1.322; $C_2{-}C_4$, 1.306; $C_4{-}H_5$, 1.093; $C_2{-}F_3$, 1.322; $C_4{-}H_6$, 1.093; $C_4C_2F_1$, 135.8; $C_2C_4H_5$, 122.5; $C_4C_2F_3$, 135.9; $C_2C_4H_6$, 122.4.

A^+ $C_2{-}F_1$, 1.293; $C_2{-}C_4$, 1.385; $C_3{-}H_5$, 1.101; $C_2{-}F_3$, 1.293; $C_4{-}H_6$, 1.101; $C_4C_2F_1$, 123.1; $C_2C_4H_5$, 121.8; $C_4C_2F_3$, 123.1; $C_2C_4H_6$, 121.8.

A^{2+} $C_2{-}F_1$, 1.274; $C_2{-}C_4$, 1.497; $C_4{-}H_5$, 1.118; $C_2{-}F_3$, 1.274; $C_4{-}H_6$, 1.118; $C_4C_2F_1$, 115.6; $C_2C_4H_5$, 121.5; $C_4C_2F_3$, 116.0; $C_2C_4H_6$, 121.5.

Furan (*A*). $O_1{-}C_2$, 1.343; $C_2{-}C_3$, 1.367; $C_3{-}C_4$, 1.456; $C_4{-}C_5$, 1.367; $C_2{-}H_6$, 1.104; $C_3{-}H_7$, 1.096; $C_4{-}H_8$, 1.096; $C_5{-}H_9$, 1.104; $O_1C_2C_3$, 110.1; $C_2C_3C_4$, 105.5; $C_3C_4C_5$, 105.5; $C_3C_2H_6$, 135.8; $C_4C_3H_7$, 126.5; $C_5C_4H_8$, 128.0; $O_1C_5H_9$, 114.1.

A^+ $O_1{-}C_2$, 1.324; $C_2{-}C_3$, 1.425; $C_3{-}C_4$, 1.398; $C_4{-}C_5$, 1.426; $C_2{-}H_6$, 1.105; $C_3{-}H_7$, 1.096; $C_4{-}H_8$, 1.096; $C_5{-}H_9$, 1.105; $O_1C_2C_3$, 109.2; $C_2C_3C_4$, 105.7; $C_3C_4C_5$, 105.8; $C_3C_2H_6$, 135.9; $C_4C_3H_7$, 128.6; $C_5C_4H_8$, 125.6; $O_1C_5H_9$, 114.9.

A^{2+} $O_1{-}C_2$, 1.314; $C_2{-}C_3$, 1.486; $C_3{-}C_4$, 1.365; $C_4{-}C_5$, 1.488; $C_2{-}H_6$, 1.117; $C_3{-}H_7$, 1.104; $C_4{-}H_8$, 1.104; $C_5{-}H_9$, 1.117; $O_1C_2C_3$, 107.4; $C_2C_3C_4$, 106.1; $C_3C_4C_5$, 106.1; $C_3C_2H_6$, 137.6; $C_4C_3H_7$, 130.0; $C_5C_4H_8$, 124.1; $O_1C_5H_9$, 115.1

Pyrrole (*A*). $N_1{-}C_2$, 1.366; $C_2{-}C_3$, 1.392; $C_3{-}C_4$, 1.433; $C_4{-}C_5$, 1.392; $C_2{-}H_6$, 1.103; $C_3{-}H_7$, 1.097; $C_4{-}H_8$, 1.098; $C_5{-}H_9$, 1.102; $N_1{-}H_{10}$, 1.021; $N_1C_2C_3$, 106.5; $C_2C_3C_4$, 107.2; $C_3C_4C_5$, 107.9; $C_3C_2H_6$, 132.2; $C_4C_3H_7$, 126.9; $C_5C_4H_8$, 125.5; $N_1C_5H_9$, 121.6; $C_2N_1H_{10}$, 123.8.

A^+ $N_1{-}C_2$, 1.357; $C_2{-}C_3$, 1.449; $C_3{-}C_4$, 1.385; $C_4{-}C_5$, 1.446; $C_2{-}H_6$, 1.105; $C_3{-}H_7$, 1.096; $C_4{-}H_8$, 1.097; $C_5{-}H_9$, 1.104; $N_1{-}H_{10}$, 1.020; $N_1C_2C_3$, 107.7; $C_2C_3C_4$, 106.5; $C_3C_4C_5$, 107.8; $C_3C_2H_6$, 130.6; $C_4C_3H_7$, 129.5; $C_5C_4H_8$, 123.4; $N_1C_5H_9$, 122.0; $C_2N_1H_{10}$, 124.4.

A^{2+} $N_1{-}C_2$, 1.408; $C_2{-}C_3$, 1.455; $C_3{-}C_4$, 1.366; $C_4{-}C_5$, 1.533; $C_2{-}H_6$, 1.114; $C_3{-}H_7$, 1.102; $C_4{-}H_8$, 1.103; $C_5{-}H_9$, 1.114; $N_1{-}N_{10}$, 1.027; $N_1C_2C_3$, 108.3; $C_2C_3C_4$, 106.5; $C_3C_4C_5$, 107.9; $C_3C_2H_6$, 131.4; $C_4C_3H_7$, 129.6; $C_5C_4H_8$, 121.6; $N_1C_5H_9$, 123.8; $C_2N_1H_{10}$, 122.3.

p-*Dihydroxybenzene* (*A*). $O_2{-}H_1$, 0.950; $O_2{-}C_3$, 1.335; $C_3{-}C_4$, 1.397; $C_4{-}H_5$, 1.104; $C_4{-}C_6$, 1.417; $C_6{-}H_7$, 1.104; $C_6{-}C_8$, 1.415; $C_8{-}O_9$, 1.329; $O_9{-}H_{10}$, 0.950; $C_8{-}C_{11}$, 1.429; $C_{11}{-}H_{12}$, 1.109; $C_{11}{-}C_{13}$, 1.375; $C_{13}{-}H_{14}$, 1.104. $C_3O_2H_1$, 111.5; $O_2C_3C_4$, 115.2; $C_3C_4H_5$, 121.3; $C_3C_4C_6$, 120.9; $C_4C_6H_7$, 119.7; $C_4C_6C_8$, 118.0; $C_6C_8O_9$, 125.5; $C_8O_9H_{10}$, 112.5; $C_6C_8C_{11}$, 120.3; $C_8C_{11}H_{12}$, 119.4; $C_8C_{11}C_{13}$, 122.6; $C_3C_{13}H_{14}$, 122.0.

A^+ $O_2{-}H_1$, 0.954; $O_2{-}C_3$, 1.283; $C_3{-}C_4$, 1.456; $C_4{-}H_5$, 1.105; $C_4{-}C_6$, 1.378; $C_6{-}H_7$, 1.103; $C_6{-}C_8$, 1.455; C_8O_9, 1.283; $O_9{-}H_{10}$, 0.954; $C_8{-}C_{11}$, 1.456; $C_{11}{-}C_{12}$, 1.104; $C_{11}{-}C_{13}$, 1.378; $C_{13}{-}H_{14}$, 1.103; $C_3O_2H_1$, 118.8; $O_2C_3C_4$, 114.6; $C_3C_4H_5$, 119.8; $C_3C_4C_6$, 121.1; $C_4C_6H_7$, 120.0; $C_4C_6C_8$, 119.0; $C_6C_8O_9$, 125.6; $C_8O_9H_{10}$, 118.9; $C_6C_8C_{11}$, 120.1; $C_8C_{11}H_{12}$, 120.3; $C_8C_{11}C_{13}$, 120.3; $C_3C_{13}H_{14}$, 120.1.

A^{2+} $O_2{-}H_1$, 0.970; $O_2{-}C_3$, 1.270; $C_3{-}C_4$, 1.495; $C_4{-}H_5$, 1.109; $C_4{-}C_6$, 1.396; $C_6{-}H_7$, 1.109; $C_6{-}C_8$, 1.429; $C_8{-}O_9$, 1.242; $O_9{-}H_{10}$, 0.971; $C_8{-}C_{11}$, 1.451; $C_{11}{-}H_{12}$, 1.111; $C_{11}{-}C_{13}$, 1.344; $C_{13}{-}C_{14}$, 1.100; $C_3O_2H_1$, 116.7; $O_2C_3C_4$, 116.7; $C_3C_4H_5$, 119.1; $C_3C_4C_6$, 121.5; $C_4C_6H_7$, 118.7; $C_4C_6C_8$, 118.7; $C_6C_8O_9$, 125.8; $C_8O_9H_{10}$, 117.8; $C_6C_8C_{11}$, 121.2; $C_8C_{11}H_{12}$, 120.4; $C_8C_{11}C_{13}$, 123.7; $C_3C_{13}H_{14}$, 120.9.

p-*Difluorobenzene* (*A*). $C_2{-}F_1$, 1.379; $C_3{-}C_2$, 1.40; $C_3{-}H_4$, 1.101; $C_3{-}C_5$, 1.410; $C_5{-}H_6$, 1.102; $C_5{-}C_7$, 1.398; $C_7{-}F_8$, 1.378; $C_7{-}C_9$, 1.402; $C_9{-}H_{10}$, 1.102; $C_9{-}C_{11}$, 1.41; $C_{11}{-}H_{12}$, 1.102; $C_3C_2F_1$, 117.9; $C_2C_3H_4$, 121.4; $C_2C_3C_5$, 117.3; $C_3C_5H_6$, 120.7; $C_3C_5C_7$, 118.7; $C_5C_7F_8$, 118.2; $C_5C_7C_9$, 123.8; $C_7C_9H_{10}$, 121.1; $C_7C_9C_{11}$, 117.8; $C_2C_{11}H_{12}$, 120.9.

A^+ $C_2{-}F_1$, 1.33; $C_3{-}C_2$, 1.433; $C_3{-}C_4$, 1.102; $C_3{-}C_5$, 1.382; $C_5{-}H_6$, 1.102; $C_5{-}H_7$, 1.439; $C_7{-}F_8$, 1.33; $C_7{-}C_9$, 1.431; $C_9{-}H_{10}$, 1.103; $C_9{-}C_{11}$, 1.384; $C_{11}{-}H_{12}$, 1.101; $C_3C_2F_1$, 117.5; $C_2C_3H_4$, 120.4; $C_2C_3C_5$, 117.1; $C_3C_5H_6$, 121.8; $C_3C_5C_7$, 119.2; $C_5C_7F_8$, 117.7; $C_5C_7C_9$, 122.6; $C_7C_9H_{10}$, 119.2; $C_7C_9C_{11}$, 119.3; $C_2C_{11}H_{12}$, 120.5.

A^{2+} $C_2{-}F_1$, 1.289; $C_3{-}C_2$, 1.487; $C_3{-}H_4$, 1.108; $C_3{-}C_5$, 1.356; $C_5{-}H_6$, 1.110; $C_5{-}C_7$, 1.479; $C_7{-}F_8$, 1.291; $C_7{-}C_9$, 1.465; $C_9{-}H_{10}$, 1.111; $C_9{-}C_{11}$, 1.363; $C_{11}{-}H_{12}$, 1.107; $C_3C_2F_1$, 120.1; $C_2C_3H_4$, 116.9; $C_2C_3C_5$, 119.3; $C_3C_5H_6$, 122.3; $C_3C_5C_7$, 118.6; $C_5C_7F_8$, 117.5; $C_5C_7H_9$, 121.4; $C_7C_9H_{10}$, 117.8; $C_7C_9C_{11}$, 120.8; $C_2C_{11}H_{12}$, 116.3.

2-*Aminoethanol* (*A*). N_4H_{10}, 1.030; $N_4{-}H_{11}$, 1.027; $N_4{-}C_3$, 1.409; $C_3{-}H_8$, 1.136; C_3H_9, 1.138; $C_3{-}C_2$, 1.495; $C_2{-}H_6$, 1.140; $C_2{-}H_7$, 2.024; $C_2{-}O_1$, 1.365; $O_1{-}H_5$, 0.995; $H_{11}N_4H_{10}$, 105.9; $H_{11}N_4C_3$, 114.4; $N_4C_3H_8$, 107.5; $N_4C_3H_9$, 114.7; $N_4C_3C_2$, 121.3; $C_3C_2H_6$, 106.6; $C_3C_2H_7$, 137.9; $C_3C_2O_1$, 121.6; $C_2O_1H_5$, 122.8.

A^+ $N_4{-}H_{10}$, 1.024; $N_4{-}H_{11}$, 1.024; $N_4{-}C_3$, 1.398; C_3H_8, 1.121; $C_3{-}H_9$, 1.123; $C_3{-}C_2$, 1.505; $C_2{-}H_6$, 1.134; $C_2{-}H_7$, 1.971; $C_2{-}O_1$, 1.341; $O_1{-}H_5$, 0.978; $H_{11}N_4H_{10}$, 109.2; $H_{11}N_4C_3$, 118.5; $N_4C_3H_8$, 111.0; $N_4C_3H_9$, 110.1; $N_2C_3C_2$, 116.9; $C_3C_2H_6$, 112.1; $C_3C_2H_7$, 143.0; $C_3C_2O_1$, 127.9; $C_2O_1H_5$, 128.9.

A^{2+} $N_4{-}H_{10}$, 1.032; $N_4{-}H_{11}$, 1.030; $N_4{-}C_3$, 1.471; $C_3{-}H_8$, 1.113; $C_3{-}H_9$, 1.116; $C_3{-}C_2$, 1.479; $C_2{-}H_6$, 1.126; $C_2{-}H_7$, 2.051; $C_2{-}O_1$, 1.390; $O_1{-}H_5$, 0.969; $H_{11}N_4H_{10}$, 107.5; $H_{11}N_4C_3$, 119.2; $N_4C_3H_8$, 116.6; $N_4C_3H_9$, 118.6; $N_4C_3C_2$, 60.0; $C_3C_2H_6$, 127.0; $C_3C_2H_7$, 142.3; $C_3C_2O_1$, 119.7; $C_2C_1H_5$, 120.3.

Butan-2-ol (*A*). $O_1{-}C_2$, 1.365; $C_2{-}C_3$, 1.535; $C_3{-}C_4$, 1.497; $C_2{-}C_5$, 1.513; $C_3{-}H_6$, 1.123; $C_2{-}H_7$, 1.145; $C_5{-}H_8$, 1.110; $C_5{-}H_9$, 1.112; $C_9{-}H_{10}$, 1.112; $C_3{-}H_{11}$, 1.122; $C_4{-}H_{12}$, 1.112; $C_4{-}H_{13}$, 1.112; $C_4{-}H_{14}$, 1.111; $O_1{-}H_{15}$, 0.951; $O_1C_2C_3$, 113.2; $C_2C_3C_4$, 109.1; $C_5C_2H_7$, 105.7; $C_4C_3H_6$. 106.2; $C_3C_2H_7$, 104.3; $C_2C_5H_8$, 114.5; $C_2C_5H_9$, 111.2; $C_2C_5H_{10}$, 114.9; $C_2C_3H_{11}$, 109.9; $C_3C_4H_{12}$, 112.2; $C_3C_4H_{13}$, 113.8; $C_3C_4H_{14}$, 113.9; $C_2O_1H_{15}$, 112.8.

A^+ $O_1{-}C_2$, 1.393; $C_2{-}C_3$, 1.471; $C_3{-}C_4$, 1.500; $C_2{-}C_5$, 1.456; $C_3{-}H_6$, 1.130; $C_2{-}H_7$, 2.04; $C_5{-}H_8$, 1.114; $C_5{-}H_9$, 1.112; $C_5{-}H_{10}$, 1.110; $C_3{-}H_{11}$, 1.121; $C_4{-}H_{12}$, 1.108; $C_4{-}H_{13}$, 1.110; $C_4{-}H_{14}$, 1.109; $O_1{-}H_{15}$, 0.971; $O_1C_2C_3$, 110.7; $C_2C_3C_4$, 103.4; $C_5C_2H_7$, 97.8; $C_4C_3H_6$, 106.4; $C_3C_2H_7$, 127.5; $C_2C_5H_8$, 113.0; $C_2C_5H_9$, 115.5; $C_2C_5H_{10}$, 110.1; $C_2C_3H_{11}$, 104.3; $C_3C_4H_{12}$, 110.1; $C_3C_4H_{13}$, 113.9; $C_3C_4H_{14}$, 113.1; $C_2O_1H_{15}$, 119.4.

A^{2+} $O_1{-}C_2$, 1.355; $C_2{-}C_3$, 1.472; $C_3{-}C_4$, 1.511; $C_2{-}C_5$, 1.454; $C_3{-}H_6$, 1.129; $C_2{-}H_7$, 2.092; $C_5{-}H_8$, 1.117; C_5H_9, 1.110; $C_5{-}H_{10}$, 1.117; $C_3{-}H_{11}$, 1.122; $C_4{-}H_{12}$, 1.109; $C_4{-}H_{13}$, 1.107; $C_4{-}H_{14}$, 1.107; $O_1{-}H_{15}$, 0.97; $O_1C_2C_3$, 114.0; $C_2C_3C_4$, 99.8; $C_5C_2H_7$, 133.3; $C_4C_3H_6$, 109.4; $C_3C_2H_7$, 92.4; $C_2C_5H_8$, 108.7; $C_2C_5H_9$, 119.9; $C_2C_5H_{10}$, 108.6; $C_2C_3H_{11}$, 102.7; $C_3C_4H_{12}$, 108.5; $C_3C_4H_{13}$, 112.8; $C_3C_4H_{14}$, 112.1; $C_2O_1H_{15}$, 126.4.

Butanal (*A*). $C_5{-}H_{11}$, 1.112; $C_5{-}C_4$, 1.498; $C_4{-}H_9$, 1.122; $C_4{-}H_{10}$, 1.120; $C_4{-}C_3$, 1.515; $C_3{-}H_7$, 1.210; $C_3{-}H_8$, 1.121; $C_3{-}C_2$, 1.494; $C_2{-}H_6$, 1.136; $C_2{-}O_1$, 1.194; $C_5{-}H_{12}$, 1.111; $C_5{-}H_{13}$, 1.111; $C_4C_5H_{11}$, 114.3; $C_5C_4H_9$, 107.9; $C_5C_4H_{10}$, 109.0; $C_5C_4C_3$, 121.5; $C_4C_3H_7$, 108.7; $C_4C_3H_8$, 108.6; $C_4C_3C_2$, 124.0; $C_3C_2H_6$, 110.0; $C_3C_2O_1$, 129.5; $C_4C_5H_{12}$, 113.6; $C_4C_5H_{13}$, 112.4.

A^+ $C_5{-}H_{11}$, 1.110; $C_5{-}C_4$, 1.499; $C_4{-}H_9$, 1.117; $C_4{-}H_{10}$, 1.116; $C_4{-}C_3$, 1.517; $C_3{-}H_7$, 1.122; $C_3{-}H_8$, 1.125; $C_3{-}C_2$, 1.464; $C_2{-}H_6$, 2.047; $C_2{-}O_1$, 1.186; $C_5{-}H_{12}$, 1.110; $C_5{-}H_{13}$, 1.106; $C_4C_5H_{11}$, 113.3; $C_5C_4H_9$, 109.5; $C_5C_4H_{10}$, 109.0; $C_5C_4C_3$, 123.1; $C_4C_3H_7$, 111.6; $C_4C_3H_8$, 111.3; $C_4C_3C_2$, 123.4; $C_3C_2H_6$, 129.5; $C_3C_2O_1$, 145.3; $C_4C_5H_{11}$, 112.4; $C_4C_5H_{13}$, 112.3.

A^{2+} $C_5{-}H_{11}$, 1.108; $C_5{-}C_4$, 1.493; $C_4{-}H_9$, 1.122; $C_4{-}H_{10}$, 1.116; $C_4{-}C_3$, 1.553; $C_3{-}H_7$, 1.128; $C_3{-}H_8$, 1.128; $C_3{-}C_2$, 1.428; $C_2{-}H_6$, 2.110; $C_2{-}O_1$, 1.149; $C_5{-}H_{12}$, 1.107; $C_5{-}H_{13}$, 1.110; $C_4C_5H_{11}$, 114.0; $C_5C_4H_9$, 112.1; $C_5C_4H_{10}$, 112.5; $C_5C_4C_3$, 122.0; $C_4C_3H_7$, 113.5; $C_4C_3H_8$, 112.9; $C_4C_3C_2$, 123.4; $C_3C_2H_6$, 179.8; $C_3C_2O_1$, 181.1; $C_4C_5H_{12}$, 112.9; $C_4C_5H_{13}$, 108.1.

2-*Propanone* (*A*). $C_3{-}C_2$, 1.501; $C_2{-}O_1$, 1.210; $C_2{-}C_4$, 1.501; $C_4{-}H_5$, 1.110; $C_4{-}H_6$, 1.110; $C_4{-}H_7$, 1.111; $C_3{-}H_8$, 1.110; $C_3{-}H_9$, 1.111; $C_3{-}H_{10}$, 1.111; $C_3C_2O_1$, 120.1; $O_1C_2C_4$, 120.3; $C_2C_4H_5$, 113.0; $C_2C_4H_6$, 113.0; $C_2C_4H_7$, 114.4; $C_2C_3H_8$, 114.0; $C_2C_3H_9$, 111 9; $C_2C_3H_{10}$, 114.5.

A^+ $C_3{-}C_2$, 1.519; $C_2{-}O_1$, 1.177; $C_2{-}C_4$, 1.519; $C_4{-}H_5$, 1.112; $C_4{-}H_6$, 1.112; $C_4{-}H_7$, 1.107; $C_3{-}H_8$, 1.111; $C_3{-}H_9$, 1.112; $C_3{-}H_{10}$, 1.107; $C_3C_2O_1$, 121.6; $O_1C_2C_4$, 121.7; $C_2C_4H_5$, 108.4; $C_2C_4H_6$, 109.1; $C_2C_4H_7$, 112.8; $C_2C_3H_8$, 110.0; $C_2C_3H_9$, 107.5; $C_2C_3H_{10}$, 112 7.

A^{2+} $C_3{-}C_2$, 1.545; $C_2{-}O_1$, 1.143; $C_2{-}C_4$, 1.543; $C_4{-}H_5$, 1.126;

C_4-H_6, 1.124; C_4-H_7, 1.122; C_3-H_8, 1.128; C_3-H_9, 1.122; C_3-H_{10}, 1.122; $C_3C_2O_1$, 145.9; $O_1C_2C_4$, 145.8; $C_2C_4H_5$, 95.7; $C_2C_4H_6$, 97.1; $C_2C_4H_7$, 150.6; $C_2C_3H_8$, 93.1; $C_2C_3H_9$, 100.2; $C_2C_3H_{10}$, 149.1.

Acetaldehyde (*A*). C_2-O_1, 1.194; C_2-H_3, 1.138; C_2-C_4, 1.477; C_4-H_5, 1.109; C_4-H_6, 1.111; C_4-H_7, 1.110; $O_1C_2H_3$, 120.9; $C_4C_2H_3$, 110.0; $C_2C_4H_5$, 115.9; $C_2C_4H_6$, 110.7; $C_2C_4H_7$, 111.8.

A^+ C_2-O_1, 1.1668; C_2-H_3, 1.167; C_2-C_4, 1.470; C_4-H_5, 1.109; C_4-H_6, 1.112; C_4-H_7, 1.109; $O_1C_2H_3$, 107.6; $C_4C_2H_3$, 110.5; $C_2C_4H_5$, 110.0; $C_2C_4H_6$, 107.8; $C_2C_4H_7$, 111.9.

A^{2+} C_2-O_1 1.144; C_2-H_3, 2.112; C_2-H_4, 1.404; C_4-H_5, 1.121; C_4-H_6, 1.121; C_4-H_7, 1.121; $O_1C_2H_3$, 0.05; $C_4C_2H_3$, 179.9; $C_2C_4H_5$, 109.7; $C_2C_4H_6$, 109.7; $C_2C_4H_7$, 109.7.

Formaldehyde (*B*). O_1-C_2, 1.181; C_2-H_3, 1.123; C_2-H_4, 1.123; $O_1C_2H_3$, 126.6; $O_1C_2H_4$, 126.6.

BH^+

O_1-C_2, 1.219; C_2-H_3, 1.111; C_2-H_4, 1.110; O_1-H_5, 0.956; $O_1C_2H_3$, 114.9; $O_1C_2H_4$, 125.1; $C_2O_1H_5$, 124.1.

BH^{2+} O_1-C_2, 1.156; C_2-H_3, 1.174; C_2-H_4, 1.174; O_1-H_5, 0.978; $O_1C_2H_3$, 126.3; $O_1C_2H_4$, 125.5; $C_2O_1H_5$, 179.6.

Ketene (*B*). O_1-C_2, 1.167; C_2-C_3, 1.312; C_3-H_4, 1.090; C_3-H_5, 1.090; $C_2C_3H_4$, 122.1; $C_2C_3H_5$, 122.2.

BH^+ O_1-C_2, 1.217; C_2-C_3, 1.285; C_3-H_4, 1.098; C_3-H_5, 1.098; O_1-H_6, 0.960; $C_2C_3H_4$, 121.5; $C_2C_3H_5$, 121.4; $C_2O_1H_6$, 120.4.

BH^{2+} O_1-C_2, 1.147; C_2-C_3, 1.375; C_3-H_4, 1.112; C_3-H_5, 1.112; O_1-H_6, 0.966; $C_2C_3H_4$, 119.8; $C_2C_3H_5$, 119.3; $C_2O_1H_6$, 177.5.

Formic acid (*B*). O_2-H_4, 0.952; O_2-C_3, 1.320; C_3-O_1, 1.204; C_3-H_5, 1.138; $C_3O_2H_4$, 118.1; $O_2C_3O_1$, 134.8; $O_2C_3H_5$, 102.3.

BH^+ O_2-H_4, 0.960; O_2-C_3, 1.264; C_3-O_1, 1.272; C_3-H_5, 1.124; O_1-H_6, 0.956; $C_3O_2H_4$, 123.7; $O_2C_3O_1$, 126.9; $O_2C_3H_5$, 111.0; $C_3O_1H_6$, 120.3.

BH^{2+} O_2-H_4, 0.982; O_2-C_3, 1.219; C_3-O_1, 1.238; C_3-H_5, 1.230; O_1-H_6, 0.974; $C_3O_2H_4$, 132.2; $O_2C_3O_1$, 145.6; $O_2C_3H_5$, 110.9; $C_3O_1H_6$, 138.9.

Methanol (*B*). O_1-H_3, 0.951; O_1-C_2, 1.340; C_2-H_4, 1.123; C_2-H_5, 1.124; C_2-H_6, 1.119; $C_2O_1H_3$, 110.9; $O_1C_2H_4$, 115.5; $O_1C_2H_5$, 111.4; $O_1C_2H_6$, 107.9.

BH^+ O_1-H_3, 0.962; O_1-C_2, 1.401; C_2-H_4, 1.112; C_2-H_5, 1.115; C_2-H_6, 1.113; O_1-H_7, 0.962; $C_2O_1H_3$, 117.1; $O_1C_2H_4$, 110.4; $O_1C_2H_5$, 104.5; $O_1C_2H_6$, 108.2; $C_2O_1H_7$, 117.2.

BH^{2+} O_1-H_3, 0.979; O_1-C_2, 1.314; C_2-H_4, 1.119; C_2-H_5, 1.189; C_2-H_6, 1.184; O_1-H_7, 0.977; $C_2O_1H_3$, 122.8; $O_1C_2H_4$, 114.4; $O_1C_2H_5$, 116.0; $O_1C_2H_6$, 114.1; $C_2O_1H_7$, 127.3.

Acetaldehyde (*B*) See earlier (*A*). BH^+ C_2-O_1, 1.243; C_2-H_3, 1.121; C_2-C_4, 1.453; C_4-H_5, 1.108; C_4-H_6, 1.112; C_4-H_7, 1.109; O_1-H_8, 0.957; $O_1C_2H_3$, 108.7; $C_4C_2H_3$, 120.7; $C_2C_4H_5$, 116.4; $C_2C_4H_6$, 108.3; $C_2C_4H_7$, 110.5; $C_2O_1H_8$, 123.9.

BH^{2+} C_2-O_1, 1.221; C_2-H_3, 1.147; C_2-C_4, 1.442; C_4-H_5, 1.188; C_4-H_6, 1.115; C_4-H_7, 1.176; O_1-H_8, 0.967; $O_1C_2H_3$, 110.9; $C_4C_2H_3$, 110.1; $C_2C_4H_5$, 127.9; $C_2C_4H_6$, 118.0; $C_2C_4H_7$, 114.2; $C_2O_1H_8$, 129.0.

Acetic acid (*B*). O_1-C_2, 1.215; C_2-O_3, 1.336; C_2-C_4, 1.497; C_4-H_5, 1.110; C_4-H_6, 1.112; C_4-H_7, 1.111; O_3-H_8, 0.948; $O_1C_2O_3$, 121.9; $O_3C_2C_4$, 115.4; $C_2C_4H_5$, 113.8; $C_2C_4H_6$, 111.9; $C_2C_4H_7$, 115.4; $C_2O_3H_8$, 118.9.

BH^+ O_1-C_2, 1.279; C_2-O_3, 1.288; C_2-C_4, 1.479; C_4-H_5, 1.109; C_4H_6, 1.111; C_4-H_7, 1.109; O_3-H_8, 0.952; O_1-H_9, 0.956; $O_1C_2O_3$, 121.0; $O_3C_2C_4$, 124.7; $C_2C_4H_5$, 114.7; $C_2C_4H_6$, 110.1; $C_2C_4H_7$, 112.3; $C_2O_3H_8$, 121.8; $C_2O_1H_9$, 124.0.

BH^{2+} O_1-C_2, 1.242; C_2-O_3, 1.265; C_2-C_4, 1.509; C_4-H_5, 1.130; C_4-H_6, 1.127; C_4-H_7, 1.125; O_3-H_8, 0.965; O_1-H_9, 0.973; $O_1C_2O_3$, 136.8; $O_3C_2C_4$, 95.9; $C_2C_4H_5$, 103.0; $C_2C_4H_6$, 105.2; $C_2C_4H_7$, 127.0; $C_2O_3H_8$, 140.7; $C_2O_1H_9$, 127.4.

Dimethyl ether (*B*). C_2-O_1, 1.342; O_1-C_3, 1.342; C_3-H_4, 1.120; C_3-H_5, 1.123; C_3-H_6, 1.124; C_2-H_7, 1.124; C_2-H_8, 1.120; C_2-H_9, 1.123; $C_2O_1C_3$, 156.7; $O_1C_3H_4$, 106.8; $O_1C_3H_5$, 115.5; $O_1C_3H_6$, 115.0; $O_1C_2H_7$, 115.1; $O_1C_2H_8$, 106.7; $O_1C_2H_9$, 115.5.

BH^+ C_2-O_1, 1.406; O_1-H_{10}, 0.963; O_1-C_3, 1.342; C_3-H_5, 1.395; C_3-H_6, 1.140; C_3-H_4, 1.554; C_2-H_8, 1.113; C_2-H_9, 1.113; C_2-H_7, 1.112; $C_2O_1H_{10}$, 109.6; $C_3O_1H_{10}$, 112.8; $O_1C_3H_5$, 115.0; $O_1C_3H_6$, 107.7; $O_1C_3H_4$, 115.6; $O_1C_2H_8$, 108.7; $O_1C_2H_9$, 110.0; $O_1C_2H_7$, 108.3.

BH^{2+} C_2-O_1, 1.457; O_1-H_{10}, 0.976; O_1-C_3, 1.314; C_3-H_5, 1.279; C_3-H_6, 1.119; C_3-H_4, 1.330; C_2-H_8, 1.116; C_2-H_9, 1.111; C_2-H_7, 1.113; $C_2O_1H_{10}$, 110.4; $C_3O_1H_{10}$, 109.8; $O_1C_3H_5$, 116.1; $O_1C_3H_6$, 120.5; $O_1C_3H_4$, 114.6; $O_1C_2H_8$, 103.0; $O_1C_2H_9$, 107.7; $O_1C_2H_7$, 106.8.

2-*Propanone* (*B*) See earlier (*A*) BH^+ C_3-C_2, 1.482; C_2-O_1, 1.262; C_2-C_4, 1.477; C_4-H_5, 1.110; C_4-H_6, 1.109; C_4-H_7, 1.108; C_3-H_8, 1.109; C_3-H_9, 1.111; C_3-H_{10}, 1.108; O_1-H_{11}, 0.956; $C_3C_2O_1$, 111.2; $O_1C_2C_4$, 121.4; $C_2C_4H_5$, 112.4; $C_2C_4H_6$, 112.4; $C_2C_4H_7$, 112.6; $C_2C_3H_8$, 114.7; $C_2C_3H_9$, 111.1; $C_2C_3H_{10}$, 111.3; $C_2O_1H_{11}$, 123.8.

BH^{2+} C_3-C_2, 1.511; C_2-O_1, 1.197; C_2-C_4, 1.532; C_4-H_5, 1.116; C_4-H_6, 1.116; C_4-H_7, 1.108; C_3-H_8, 1.118; C_3-H_9, 1.117; C_3-H_{10}, 1.111; O_1-H_{11}, 0.956; $C_3C_2O_1$, 120.9; $O_1C_2C_4$, 123.4; $C_2C_4H_5$, 105.0; $C_2C_4H_6$, 105.2; $C_2C_4H_7$, 114.5; $C_2C_3H_8$, 107.3; $C_2C_3H_9$, 106.3; $C_2C_3H_{10}$, 114.1; $C_2O_1H_{11}$, 159.5.