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Relative responses of various classes of compounds using a pulsed discharge helium photoionization detector
Experimental determination and theoretical calculations

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Abstract

The relative response factors for 174 compounds have been determined using a helium pulsed discharge photoionization detector. The values were obtained with a relative standard deviation that ranged to 4.3% with a median of 1%. The mean values of the relative mass response factors ranged from 0.26 to 1.18. If the detector is not calibrated and equal response factors are assumed, a potential error of $\pm 32\%$ could be expected. The SCF molecular orbitals of these same molecules were calculated and used to determine the number of ionizable electrons based upon the He_2 continuous emission. The molar response of the compounds and the number of ionizable electrons are well correlated.

Keywords: Detection, GC; Pulsed discharge helium photoionization detection; Photoionization detection

1. Introduction

The pulsed discharge helium ionization detector (PDHID) was introduced in 1992 [1]. The configuration used in the initial paper allowed the sample to pass through the discharge. The electrons were collected by applying the bias potential across the discharge region. This configuration gave unparalleled sensitivity to permanent gases and a linear dynamic range of more than three orders of magnitude. However, the analysis of organic compounds could not be performed satisfactorily since carbon was deposited on the platinum electrodes.

An alternative configuration was given in a later

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paper [2] in which the gas chromatography (GC) eluent was introduced into the detector downstream from the discharge region. The ionization of the eluents occurred via photoionization using the He_2 vacuum UV continuum. This radiation is of sufficiently high energy that all compounds, including the inert gases, except for neon, are photoionized. The PDHID is a truly universal detector capable of detecting H_2, O_2, CO, CO_2, H_2O as well as organic compounds ranging from light hydrocarbons to high molecular weight pesticides and metal complexes.

In later publications [3,4] argon and krypton doped helium were used as the discharge gas. The energy of the discharge which is deposited in different excited states in helium [5] is then transferred to argon or krypton. The emission then arises

from the resonance lines of the elements and the diatomic species Ar_2 and Kr_2. These detectors have been called pulsed discharge photoionization detectors (PDPID) with a dopant as a prefix, such as Kr-PDPID. The PDHID then could also be called a He-PDPID.

The two purposes of this paper are (1) to measure the response of a variety of organic compounds to see how much the response varies on a per mass basis and (2) to carry out quantum mechanical calculations on these same organic compounds to see if the response per mole (res/mol) is related to the number of ionizable electrons. Since all elements in a compound can be ionized by the high energy He_2 emission, perhaps the response on a per mass basis could be sufficiently constant that an approximate concentration could be calculated without prior calibration. It is well known that photons of sufficiently high energy are capable of ionizing any electrons in molecular orbitals of lower energy. This is the basic premise of photoelectron spectroscopy. The present calculations will establish a rationale for the response of the PDHID and give a basis for approximating the response for a specific compound. This will be limited by the accuracy of the quantum mechanical calculations and the naive assumption that all electrons in the sufficiently low energy molecular orbitals have the same photoionization cross section.

Some information on the first objective was presented in an earlier publication [2]. It was noted that the saturated hydrocarbons had a similar response per gram which is analogous to the response from a flame ionization detector (FID) where the response depends approximately upon the number of carbon atoms in the molecule. No adequate explanation for this observation was presented. A rationale for the responses of not only saturated hydrocarbons but also unsaturated and aromatic hydrocarbons and compounds containing heteroatoms and functional groups will be presented. Generally a high response for aromatics is associated with a photoionization detector which uses a krypton source. However, with the PDHID the response to benzene is less than that of hexane. The results of this study will give a logical explanation for this result. In a subsequent paper we will consider the responses of organic compounds using the Kr-PDPID [9].

2. Experimental

The schematic diagram and configuration of the detector used throughout this work is similar to the one described previously [2] with two modifications. First, quartz is used to replace vespel as an insulator since vespel tends to decompose and reduce the response at higher temperatures. Quartz also has a
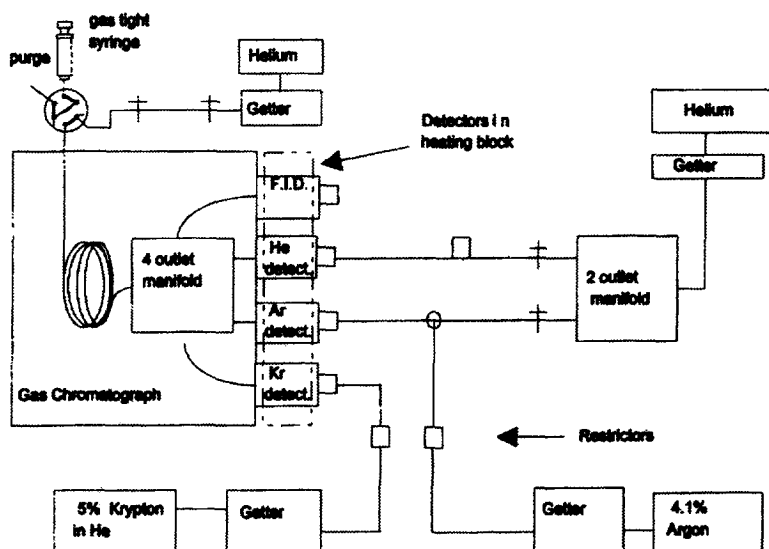

Fig. 1. Block diagram of the experimental system.

lower electrical conductivity. The second modification was the enlargement of the discharge section by using a 3 mm internal diameter instead of 1.6 mm. In addition to these slight changes in configuration, the bias voltage was increased to 600 V to ensure complete collection of electrons.

A block diagram of the complete system is shown in Fig. 1. Grade five nines helium gas was passed through a helium purifier (Valco Instruments, Houston, TX, USA) at the "bake out" position (673 K) and was used both as the carrier gas and the make up gas. Flow control was accomplished by using needle valves. The ignition coil and the driver circuitry for generating the high-voltage discharge were contained in a shielded aluminum box and powered with a 20 V d.c. potential using a Heath 2718 tri-power supply (Heath Company, Benton Harbor, MI, USA). The pulse width of 40 μs and the pulse period of 300 μs were controlled with a 4001 ultravariable pulse generator (Global Specialties, New Haven, CT, USA). The bias potential of 600 V d.c. applied to the electrode nearest to the discharge was supplied by a Keithley Model 240 A high-voltage power supply (Keithley Instruments, Cleveland, OH, USA) or a Nepco ABC 1500 V supply (Kepco, Flushing, NY, USA). The signal was then sent to the electrometer of the Varian Aerograph 1400 GC (Varian, Flushing, NY, USA) and recorded by a Spectra-Physics SP 4400 integrator (Spectra-Physics, San Jose, CA, USA). The detector was heated by three heating cartridges (Model C 245, Watlow Electric, St. Louis, MO, USA) connected to a Variac power supply (Model 116B, Superior Electric, Bristol, CT, USA). The detector was heated to a temperature of 90°C to prevent condensation of samples. The temperature of the detector was monitored by a thermocouple (K type, Omega Engineering, Stanford, CT, USA) which was connected to a digital temperature readout (Omega Digicator Model 400, Omega Engineering).

A HP 5790A GC (Hewlett-Packard, Avondale, PA, USA) was used with a 30 m DB-5 column (J&W Scientific, Folsom, CA, USA). The chromatograph was also equipped with a four-port gas sampling valve containing a 10-μl external sampling loop and a four port liquid sampling valve with a 0.06-μl internal sampling loop. The liquid valve was heated to a temperature of 44°C to assist in the vaporization of the solvent from the solutions in the same fashion

as mentioned above. The temperature program was as follows: 30°C for 8 min, 5°C/min ramp to 120°C and held for 8 min. The flow-rate of helium through the column was 1 ml/min while the flow-rate of helium make up gas passing through the discharge region (normally 30 ml/min) was controlled by a pressure regulator at 25–30 p.s.i. (1 p.s.i.=6894.76 Pa) through a fixed restrictor. The column flow-rate of helium which passes through both the gas and liquid valves was regulated by two needle valves in series.

Two experimental procedures were used based on the volatility of the compounds. Volatile compounds (b.p. less than 100°C) were introduced through the gas valve with a 10-μl external loop. Nonvolatile compounds (b.p. greater than 100°C) were introduced through the liquid valve with a 0.06-μl internal loop. The classes of analytes were saturated hydrocarbons, aromatics, alcohols, alkenes, alkynes, ketones, aldehydes, halogenated compounds, sulfur compounds, amines, amides and nitriles. The chemicals were purchased in 99% purity from Aldrich (Milwaukee, WI, USA) and were used as received.

Gaseous mixtures were prepared by introducing a known volume of liquid with a 10-μl syringe into a modified 250-ml Erlenmeyer flask which was first purged with helium for approximately half a day. The flask was modified to accept two half hole cylindrical septa (Altech Associates, Deerfield, IL, USA), one for sample introduction and the other for sample removal. The flask was heated for about 2 to 3 h so that a maximum amount of the analyte was vaporized. A known volume of an internal standard, hexane, was also injected into the flask. The vapor of the mixtures in the flask was then introduced into an external 10-μl sample loop. The amount of analyte injected into the flask was 1.0 μl.

The relative responses on both a mass basis and a mole basis were calculated from the ratio of the relative areas of each compound to hexane and the known relative amounts of the sample and standard by:

$$\text{Relative response} = \frac{\text{Response of compound}}{\text{Response of hexane}}$$
$$\text{(mass basis)}$$
$$\times \frac{\text{Grams of hexane}}{\text{Grams of compound}}$$

Relative response = Relative response
   (molar basis)   (mass basis)

$$\times \frac{\text{Molecular wt. of compound}}{\text{Molecular wt. of hexane}}$$

Liquid sample mixtures of analytes were prepared by dissolving a known amount of analyte into a known volume of carbon disulfide. The mass basis and the mole basis response were then calculated as described above.

2.1. Calculation of ionizable electrons

The quantum mechanical calculations were carried out using a commercial program called HyperChem (Hypercube, Waterloo, Canada). This is a molecular modeling and simulation program that has some of the following functions: (i) drawing molecular structure from atoms and converting them to a three dimensional model; (ii) performing various complex chemical calculations including semiempirical quantum mechanical methods and molecular dynamics; (iii) running HyperChem repeatedly with a script menu on different molecules and (iv) integrating HyperChem with other available software. The HyperChem program was used in this study to calculate the number of electrons of different classes of organic compounds which are ionizable by the He_2 continuum. The calculations were done through the semiempirical SCF quantum mechanical method using the AM1 (Austin Model 1) model and parameters. This is useful for the calculations of organic molecules containing elements containing the main group elements. For example, the electron affinities and ionization potentials of the purines and pyrimidines in DNA and RNA have been calculated in good agreement with experimental values [6]. It optimizes the geometry and calculates the molecular orbital energies for all of the valence electrons. These can be used to obtain the number of electrons ionizable by the He_2 continuum in a molecule.

The radiation emitted from the discharge in pure helium arises from a He_2 eximer state($^1\Sigma_u^+$) and the transition to the dissociative ground state gives radiation in the range 57–110 nm, the well known Hopfield emission, first observed by Hopfield [7] and later investigated by Tanaka and co-workers [8].

Tanaka reported the intensity distribution in the continua of all the inert gases. The photons of the He_2 continuum have a high energy and large span and are capable of ionizing any compounds making the PDHID response universal. The fraction of the photons that are available with the same or higher energy than the electrons in a certain energy level must be very precisely calculated. This fraction of photons can potentially ionize the electrons in that particular energy level. By multiplying the fraction of the photons times the number of electrons with that energy we get the possibility of ionizing those electrons.

The first step in the calculation of the ionizable electrons is to obtain the emission spectra of the He_2 continuum (Fig. 2) as a function of wave length. This emission spectra was monitored in the vacuum UV region (57–200 nm). The vacuum monochromator used was an Acton VM 502 (Acton Research, Acton, MA, USA) with an optimum wavelength range in the vacuum UV region. It had a focal length of 0.2 m and an aperture ratio of 4.5. A 1200 g/mm holographic grating with a dispersion of 4 nm/mm and an operating range of 30 nm to 550 nm was used. The exit slit was set at 0.1 mm and the resolution could not be better than 0.4 nm. Instead of an entrance slit the discharge itself was used as the optical image. The cell was made so that the discharge occurred at the focal point where the entrance slit would normally be located. The vacuum UV radiation was converted to UV radiation by a sodium methylsalicylate phosphor deposited on a
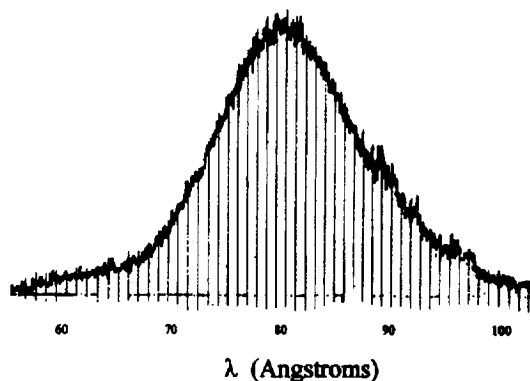

Fig. 2. Emission spectra of the He_2 continuum: intensity versus wavelength.

plate in front of the photomultiplier tube (PMT). An EMI 9781B PMT (EMI Gencom, NY, USA) was used. The spectrum of the He_2 continuum which had a wavelength range from 57–110 nm was obtained using a windowless PDED by purging the mono-chromator with helium in order to maintain trans-parency down to 57 nm.

The second step involved the conversion of wave-length into energy by using the equation $E = hc/\lambda$. The wavelength range used was from 57–107 nm and the corresponding energy range is from 21.69 eV to 11.55 eV. The intensities and the energies obtained from above were then used to obtain a plot of intensity versus energy, as shown in Fig. 3. This plot looks very similar to the spectra of the He_2 con-tinuum; the only difference being that it is skewed on the high energy side.

The intensity versus energy curve is then inte-grated using the trapezoid approximation. The area for each trapezoidal segment is first evaluated. These area segments are then summed to give the total area
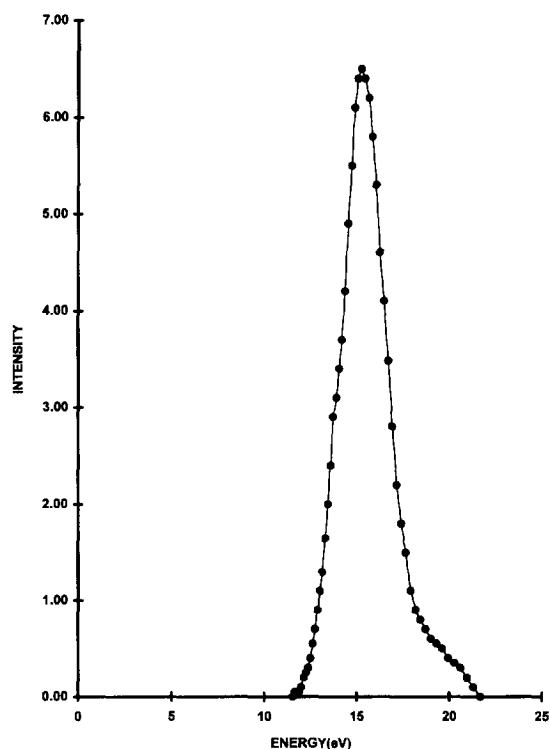

Fig. 3. Emission spectra of the He_2 continuum: intensity versus energy.

under the curve. The fraction of the radiation which has a specified energy and above is then obtained by summing up the trapezoidal areas from 21.69 eV to the designated energy and dividing by the total area. A table of these fractions, F_i, at the specified energies are given in Table 1. A graph of F_i versus energy (eV) is given in Fig. 4.

The eigenvalues obtained from HyperChem give the energies of the filled orbitals that contain elec-trons which are ionizable by the He_2 continuum. Only the negative energies are used since they represent the filled orbitals. All the orbitals at energies ranging from the highest negative value to -21.69 eV are taken into account because the He_2 continuum ranges from -21.69 eV to -11.55 eV. The electrons in the orbitals higher than -11.55 eV are assumed to be ionized by 100% of the photons from the He_2 continuum.

The plot of F_i versus energy in Fig. 4 gives the fraction of the photons that are capable of ionizing the electrons in orbitals whose values are determined from the HyperChem calculations. Electrons having orbital energies that fall within the distribution but lower than -11.60 eV have only a fraction of the photons which are capable of ionizing them. We assume they have the same potential of ionization as other electrons which lie in orbitals having higher energies and are outside the distribution e.g. greater than -11.55 eV.

The fraction of the photons corresponding to each energy from -7 eV to -21.69 eV is then added up and the total fraction of the photons utilized to ionize all the filled orbitals up to -21.69 eV is obtained. The total fraction of the photons is then multiplied by two since there are two electrons in each orbital, thus enabling us to obtain the total number of electrons in the organic molecules ionizable by the He_2 continuum. The results showing the number of ionizable electrons for each molecule and the re-sponse on a mole basis are shown in Table 2.

3. Results and discussion

The experimental results for 174 compounds are given in Table 2. The calculated values of the number of ionizable electrons is given in the last column. These average values for different groups

Table 1
The fraction of the photons in the helium excimer continuum with energy greater than E_i

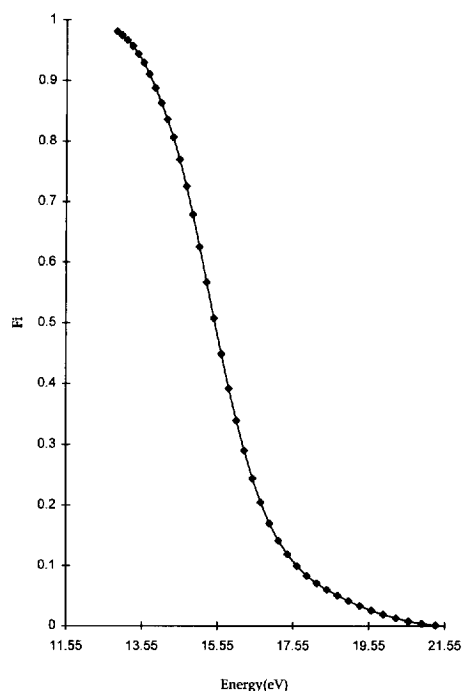| Energy	F_i
21.31	0.0009
20.95	0.0034
20.60	0.0075
20.27	0.0126
19.94	0.0185
19.62	0.0253
19.32	0.0328
19.02	0.0409
18.73	0.0499
18.45	0.0598
18.18	0.0707
17.92	0.0831
17.66	0.0991
17.41	0.1187
17.17	0.1415
16.93	0.1700
16.70	0.2044
16.48	0.2441
16.26	0.2896
16.05	0.3389
15.85	0.3916
15.65	0.4486
15.45	0.5075
15.26	0.5667
15.07	0.6248
14.89	0.6783
14.72	0.7251
14.54	0.7696
14.37	0.8063
14.21	0.8363
14.05	0.8633
13.89	0.8880
13.73	0.9108
13.58	0.9297
13.44	0.9443
13.29	0.9572
13.15	0.9670
13.01	0.9750
12.88	0.9812
12.74	0.9865
12.61	0.9904
12.48	0.9933
12.36	0.9952
12.24	0.9968
12.12	0.9981
12.00	0.9990
11.88	0.9994
11.77	0.9996
11.66	0.9999
11.55	1.0000

Fig. 4. Fractional energy, F_i, of the He_2 continuum, with energy greater than E_i, versus E_i.

are given in Table 3. The slopes of the molar response versus the number of ionizable electrons are shown in Table 4. Fig. 5, Fig. 6 and Fig. 7 present representative molecular orbital diagrams which were used to calculate the number of ionizable electrons. Fig. 8, Fig. 9, Fig. 10 and Fig. 11 indicate the correlation between the responses for several classes of molecules as a function of the number of ionizable electrons.

3.1. Experimental response factors

Table 2 shows the mean of the ratios of the areas for each compound relative to hexane. The reported value is the average of at least five runs. It also shows the standard deviation, the percent standard deviation, the response on a mass basis and the response on a mole basis.

The percent standard deviation is a measure, in part, of the reproducibility of the detector. The variation in these repetitive injections and measurement of peak areas arise from errors in the detector and errors in the integration. Variations in the amount

Table 2
Relative response factors and number of ionizable electrons

Compound		Mean	S.D.	% S.D.	Res/g	Res/mol	Number of ionizable electrons
Hydrocarbons							
Linear hydrocarbons							
1	Hexane	1	0	0	1.000	1.000	22.0
2	Pentane	1.126	0.022	1.957	1.185	0.992	18.7
3	Heptane	0.977	0.006	0.585	0.941	1.095	25.3
4	Octane	0.986	0.013	1.267	0.925	1.225	28.6
5	Nonane	0.984	0.017	1.737	0.903	1.344	32.0
6	Decane	0.858	0.022	2.542	0.774	1.278	35.4
Cyclic Hydrocarbons							
7	Cyclopentane	1.119	0.013	1.190	0.982	0.799	16.5
8	Cyclohexane	1.186	0.010	0.847	1.004	0.980	20.3
9	Cycloheptane	0.938	0.036	3.834	0.762	0.868	23.5
10	Cyclooctane	1.148	0.017	1.488	0.907	1.181	26.7
11	Methyl cyclopentane	0.853	0.005	0.558	0.751	0.733	20.2
12	1,1-Dimethylcyclohexane	0.997	0.039	3.871	0.846	1.101	27.5
13	Ethylcyclohexane	1.146	0.033	2.917	0.958	1.248	27.3
14	Propylcyclohexane	1.180	0.041	3.460	0.981	1.436	30.5
Branched Hydrocarbons							
15	3,3-Dimethylpentane	1.113	0.013	1.131	1.058	1.230	25.7
16	3,3-Diethylpentane	0.827	0.015	1.857	0.726	1.081	32.8
17	2-Methylhexane	0.993	0.004	0.358	0.964	1.121	25.5
18	3-Methylhexane	1.113	0.006	0.499	1.068	1.242	25.6
19	2-Methylheptane	1.019	0.009	0.867	0.962	1.275	28.9
20	2,3-Dimethylpentane	1.116	0.008	0.714	1.058	1.231	25.8
21	2,4-Dimethylpentane	1.011	0.003	0.313	0.990	1.151	25.9
22	2,4-Dimethylhexane	1.033	0.006	0.624	0.971	1.287	29.1
23	2,3,4-Trimethylpentane	1.103	0.007	0.664	1.010	1.339	29.5
24	2,2,4-Trimethylpentane	1.055	0.013	1.224	1.005	1.332	29.5
25	2,2,4,4-Tetramethylpentane	1.070	0.018	1.706	0.981	1.460	35.3
Aromatic hydrocarbons							
26	Benzene	0.974	0.005	0.463	0.734	0.665	13.2
27	Toluene	0.833	0.010	1.252	0.635	0.679	18.7
28	Ethylbenzene	0.839	0.014	1.658	0.638	0.786	21.9
29	Propylbenzene	0.934	0.013	1.414	0.714	0.995	25.7
30	*sec.*-Butylbenzene	0.630	0.014	2.282	0.481	0.750	29.0
31	*n*-Butylbenzene	0.534	0.014	2.640	0.409	0.638	28.6
32	3-Ethyltoluene	0.668	0.017	2.559	0.509	0.709	29.1
33	*o*-Xylene	0.696	0.022	3.128	0.527	0.650	22.3
34	*m*-Xylene	0.752	0.006	0.798	0.571	0.703	22.4
35	*p*-Xylene	0.870	0.020	2.243	0.662	0.816	22.4
36	Cumene	1.025	0.006	0.593	0.782	1.090	25.6
37	Mesitylene	1.077	0.008	0.701	0.821	1.145	24.4
Alcohols							
38	1-Propanol	0.893	0.013	1.410	0.732	0.510	13.1
39	2-Propanol	0.905	0.010	1.105	0.760	0.530	13.5
40	1-Butanol	0.815	0.013	1.584	0.663	0.570	16.5
41	1-Pentanol	0.439	0.013	2.997	0.357	0.365	19.8
42	2-Pentanol	0.564	0.011	1.985	0.458	0.468	20.3

(Contd.)

Table 2 (Contd.)

Compound		Mean	S.D.	% S.D.	Res/g	Res/mol	Number of ionizable electrons
43	1-Hexanol	0.525	0.013	2.459	0.425	0.504	23.1
44	2-Hexanol	0.588	0.012	1.994	0.479	0.567	23.7
45	1-Heptanol	0.660	0.018	2.766	0.529	0.713	26.5
46	sec.-Butanol	0.748	0.013	1.683	0.610	0.524	17.1
47	Isobutanol	0.726	0.010	1.426	0.595	0.512	16.8
48	2-Methyl-1-butanol	0.755	0.020	2.688	0.613	0.627	20.2
49	2-Methyl-2-butanol	0.981	0.001	0.098	0.803	0.821	20.7
50	3-Methyl-2-butanol	0.550	0.016	2.969	0.448	0.458	20.1
51	2-Methyl-1-pentanol	0.374	0.011	2.985	0.299	0.355	23.5
52	2-Methyl-2-pentanol	1.024	0.009	0.861	0.808	0.958	24.1
53	2-Methyl-3-pentanol	0.782	0.010	1.326	0.629	0.746	24.0
54	2-Methyl-2-hexanol	1.045	0.007	0.666	0.848	1.143	27.1
55	3-Methyl-2-butanol	0.814	0.009	1.076	0.656	0.671	20.6
56	3-Methyl-1-pentanol	0.657	0.007	1.017	0.526	0.624	23.3
57	4-Methyl-2-pentanol	0.663	0.008	1.274	0.545	0.646	24.0
58	6-Methyl-2-heptanol	0.735	0.006	0.801	0.603	0.912	30.3
59	Cyclohexanol	0.579	0.023	3.953	0.396	0.460	21.8
Ketones							
60	Acetone	0.768	0.010	1.247	0.639	0.431	11.8
61	Methylethyl ketone	0.685	0.017	2.529	0.561	0.469	15.0
62	2-Pentanone	0.771	0.008	1.085	0.626	0.625	18.4
63	3-Pentanone	0.788	0.015	1.905	0.608	0.608	18.5
64	2-Hexanone	0.721	0.005	0.739	0.585	0.680	21.6
65	2-Heptanone	0.640	0.014	2.210	0.517	0.686	25.2
66	4-Heptanone	0.680	0.014	2.080	0.548	0.727	24.7
67	3-Methyl-2-butanone	0.795	0.006	0.802	0.651	0.650	18.7
68	3,3-Dimethyl-2-butanone	0.890	0.014	1.589	0.732	0.851	20.9
69	4-Methy-2-pentanone	0.815	0.017	2.125	0.671	0.779	22.0
70	2,2,4,4-Tetramethyl-3-pentanone	0.825	0.013	1.565	0.660	1.089	31.3
71	2-Methyl-3-pentanone	0.924	0.008	0.815	0.751	0.873	20.1
72	2-Methyl-3-hexanone	0.783	0.010	1.224	0.625	0.828	25.4
73	2-Methyl-3-heptanone	0.827	0.008	1.012	0.668	0.994	28.7
74	3-Methyl-2-pentanone	0.879	0.005	0.517	0.711	0.826	22.0
75	4-Methyl-2-pentanone	0.905	0.005	0.499	0.744	0.865	22.1
76	2-Methyl-cyclohexanone	0.929	0.007	0.733	0.662	0.862	23.3
77	3-Methyl-cyclohexanone	0.926	0.006	0.594	0.666	0.867	23.1
78	4-Methyl-cyclohexanone	0.852	0.005	0.586	0.614	0.799	23.1
79	Cyclopentanone	0.765	0.009	1.200	0.530	0.517	16.6
80	Cyclohexanone	0.695	0.013	1.858	0.484	0.551	19.7
81	2,3-Butanedione	0.708	0.005	0.707	0.475	0.475	14.9
82	3,4-Hexanedione	0.708	0.007	0.967	0.497	0.658	21.6
Alkenes							
83	1-Hexene	0.983	0.022	2.257	0.962	0.940	20.0
84	1-Heptene	0.947	0.006	0.654	0.895	1.020	23.3
85	cis-2-Heptene	0.896	0.009	1.016	0.834	0.950	23.6
86	trans-2-Heptene	0.905	0.006	0.651	0.851	0.969	23.7

Compound		Mean	S.D.	% S.D.	Res/g	Res/mol	Number of ionizable electrons
87	1-Octene	0.710	0.015	2.086	0.655	0.852	24.7
88	*trans*-2-Octene	0.994	0.006	0.575	0.912	1.188	27.1
89	1-Nonene	0.856	0.011	1.333	0.773	1.132	30.0
90	2,3,3-Trimethyl-1-butene	0.779	0.011	1.376	0.728	0.830	24.4
91	2-Methyl-1-hexene	0.815	0.013	1.641	0.771	0.878	23.5
92	3-Methyl cyclopentene	0.803	0.005	0.623	0.545	0.520	18.6
93	1-Methyl cyclohexene	0.673	0.011	1.695	0.546	0.609	22.2
Alkynes							
94	1-Hexyne	0.750	0.007	0.926	0.691	0.659	18.4
95	2-Hexyne	0.788	0.029	3.662	0.710	0.677	18.8
96	3-Hexyne	0.760	0.013	1.686	0.693	0.661	18.7
97	1-Heptyne	0.768	0.014	1.768	0.690	0.770	21.8
98	1-Octyne	0.833	0.018	2.127	0.735	0.940	25.1
Ethers							
99	Dipropyl ether	0.925	0.018	1.968	0.828	0.982	23.2
100	Diethyl ether	1.042	0.014	1.323	0.970	0.834	16.8
101	*n*-Dibutyl ether	0.698	0.011	1.626	0.602	0.910	29.9
102	Methyl *tert.*-butyl ether	0.972	0.006	0.588	0.866	0.885	20.5
103	Isobutylvinyl ether	0.897	0.009	1.058	0.770	0.895	21.7
104	THF	0.865	0.017	2.002	0.641	0.537	17.8
105	Propylene oxide	1.125	0.038	3.365	0.893	0.602	11.4
Esters							
106	Propyl acetate	0.700	0.015	2.081	0.520	0.616	20.2
107	Isopropyl acetate	0.870	0.005	0.574	0.658	0.779	20.8
108	Butyl acetate	0.875	0.007	0.795	0.653	0.881	23.5
109	Isobutyl acetate	0.817	0.010	1.270	0.620	0.836	23.8
110	Ethyl propionate	0.916	0.013	1.452	0.677	0.803	19.8
111	Ethyl butyrate	0.956	0.012	1.270	0.718	0.967	23.6
112	Ethyl caproate	0.920	0.014	1.513	0.694	1.162	29.6
113	Methyl propionate	0.853	0.007	0.803	0.614	0.628	16.4
114	Methyl-3-butenoate	0.726	0.005	0.716	0.509	0.592	17.3
115	Methyl caproate	0.913	0.010	1.122	0.680	1.027	25.9
116	Methyl enanthate	0.822	0.011	1.359	0.623	1.042	29.9
117	Propyl butyrate	0.903	0.013	1.402	0.681	1.029	26.3
118	Isopropyl butyrate	0.919	0.007	0.769	0.705	1.065	27.3
119	Propyl formate	0.811	0.006	0.749	0.591	0.605	16.2
120	Butyl formate	0.861	0.013	1.518	0.636	0.754	19.8
Aldehydes							
121	Butyraldehyde	0.481	0.001	0.199	0.396	0.331	14,5
122	Valaraldehyde	0.320	0.008	2.552	0.260	0.260	17.8
123	Isovalaraldehyde	0.914	0.011	1.200	0.750	0.749	18.1
124	Hexanal	0.914	0.007	0.718	0.722	0.839	21.1
125	Heptaldehyde	0.897	0.006	0.711	0.723	0.958	22.5
126	Octylaldehyde	0.777	0.008	1.043	0.623	0.928	27.7
127	2-Ethylbutyraldehyde	0.770	0.012	1.623	0.624	0.725	21.5
128	2-Ethylhexanal	0.501	0.020	3.915	0.402	0.598	21.2
129	2-Methyl-2-butenal	0.862	0.008	0.910	0.652	0.637	16.9
130	2-Methyl valaraldehyde	0.914	0.007	0.718	0.745	0.866	21.4
131	3-Methyl-2-butanal	0.709	0.011	1.613	0.536	0.523	18.7

Table 2 (Contd.)

Compound		Mean	S.D.	% S.D.	Res/g	Res/mol	Number of ionizable electrons
Halogens							
Chloro compounds							
132	Chlorobenzene	0.872	0.005	0.570	0.519	0.678	17.8
133	1,2-Dichlorobenzene	0.797	0.023	2.944	0.402	0.686	20.4
134	1,4-Dichlorobutane	0.809	0.011	1.375	0.459	0.677	19.8
135	Carbon tetrachloride	1.128	0.022	1.967	0.466	0.832	18.1
136	Trichloroethylene	1.178	0.008	0.709	0.531	0.809	14.8
137	Tetrachloroethylene	0.890	0.037	4.103	0.362	0.696	17.7
138	Cyclopentylchloride	1.403	0.034	2.427	0.460	0.558	19.5
Bromo compounds							
139	Dibromomethane	0.688	0.021	2.999	0.183	0.369	11.2
140	1,2-Dibromoethane	1.061	0.010	0.979	0.160	0.349	14.4
141	1-Bromobutane	1.173	0.021	1.758	0.303	0.482	18.2
142	1-Bromopentane	0.610	0.024	4.016	0.330	0.578	21.5
143	1-Bromohexane	0.866	0.013	1.497	0.485	0.930	24.8
144	1,2-Dibromoethylene	1.220	0.037	3.067	0.179	0.384	12.9
145	Bromoform	0.930	0.014	1.460	0.212	0.621	14.1
Iodo compounds							
146	Iodomethane	1.895	0.017	0.914	0.548	0.902	9.0
147	1-Iodobutane	1.793	0.035	1.953	0.365	0.779	18.5
Fluoro compounds							
148	2,2,2-Trifluoroethanol	0.643	0.017	2.658	0.308	0.415	12.8
149	1,4-Difluorobenzene	1.528	0.017	1.118	0.453	0.600	16.3
150	*m*-Fluorotoluene	1.238	0.030	2.413	0.411	0.525	19.4
151	*o*-Fluoroanisole	0.699	0.003	0.379	0.410	0.599	20.4
152	*m*-Fluoroanisole	0.582	0.014	2.455	0.348	0.509	19.9
153	*p*-Fluoroanisole	0.529	0.004	0.792	0.313	0.458	20.4
Nitriles							
154	Acetonitrile	0.840	0.014	1.652	0.704	0.335	8.1
155	Trimethylacetonitrile	0.889	0.011	1.217	0.779	0.751	17.0
156	Acrylonitrile	0.593	0.014	2.419	0.485	0.298	9.8
157	Propionitrile	0.619	0.011	1.752	0.528	0.338	11.4
158	Isobutyronitrile	0.484	0.016	3.261	0.419	0.336	15.1
159	Butyronitrile	0.880	0.007	0.827	0.730	0.586	14.8
Sulfur compounds							
160	Carbon disulfide	1.793	0.055	3.068	0.933	0.824	10.4
161	Ethyl sulfide	1.116	0.008	0.695	0.879	0.920	18.3
162	Propyl sulfide	1.080	0.046	4.273	0.849	1.165	25.0
163	Ethyl disulfide	1.059	0.008	0.711	0.703	0.997	21.8
164	1-Pentanethiol	1.122	0.008	0.703	0.880	1.064	21.4
165	1-Hexanethiol	1.182	0.006	0.528	0.929	1.275	24.7
Miscellaneous							
166	Nitromethane	0.745	0.019	2.570	0.436	0.324	9.0
167	Nitroethane	0.985	0.029	2.901	0.621	0.541	12.2
168	Pyridine	0.378	0.014	3.785	0.255	0.234	13.9
169	Triethylamine	0.334	0.012	3.623	0.303	0.356	24.6
170	N-Methylpropionamide	0.371	0.014	3.837	0.263	0.265	17.6
171	Anisole	0.654	0.004	0.535	0.433	0.544	19.6
172	2,4-Dimethylbenzaldehyde	0.831	0.010	1.195	0.569	0.886	25.5
173	2,5-Dimethylbenzaldehyde	0.868	0.009	1.092	0.602	0.937	25.4
174	Benzaldehyde	0.446	0.012	2.770	0.282	0.347	18.1

Table 3

Mean relative response/gram for each class of compounds

	Classes	Range of res/g	Mean of res/g	S.D.	% S.D.	No. of compounds
1	Saturated Hydrocarbons	0.72–1.18	0.946	0.108	11.4	25
2	Aromatics	0.40–0.82	0.624	0.127	20.4	11
3	Alcohols	0.30–0.84	0.581	0.151	25.9	22
4	Ketones	0.47–0.75	0.619	0.128	27.9	23
5	Alkenes	0.54–0.96	0.77	0.141	18.3	11
6	Alkynes	0.69–0.73	0.704	0.019	2.7	5
7	Ethers	0.64–0.97	0.796	0.156	19.6	7
8	Esters	0.51–0.71	0.639	0.062	9.7	15
9	Aldehydes	0.26–0.75	0.563	0.167	29.6	11
10	Halogens	0.16–0.55	0.373	0.113	30.4	22
	Chloro	0.36–0.53	0.457	0.060	13.1	7
	Bromo	0.16–0.48	0.265	0.117	44.2	7
	Iodo	0.36–0.55	0.456	0.129	28.3	2
	Fluoro	0.41–0.45	0.373	0.037	10.0	6
11	Nitriles	0.42–0.77	0.608	0.149	24.5	6
12	Sulfur Compounds	0.70–0.93	0.858	0.081	9.5	6
	All classes	0.16–1.18	0.647	0.207	32.0	174

injected are not relevant since the ratio of the area of a compound to that of hexane was taken. Also errors in sample preparation would not influence this error since all injections were made from the same solution. Assuming the integration is sufficiently precise, these percent standard deviations reflect the reproducibility of the detector. For relatively sharp or narrow peaks this is probably true, but when the peaks are broad and/or tail significantly, the error in the integration would be significant. Since a nonpolar GC column was used, tailing will occur for the more polar compounds such as alcohols, nitriles, nitro compounds, and amines. The lower errors which are on the order of 0.5–1% reflect the detector precision and are consistent with previous studies [2].

Table 4

Summary of slopes obtained by correlating the molar responses with the number of ionizable electrons

|	Classes	R^2	Linearity	Slope	Number of compounds
1	Saturated hydrocarbons	0.8310	Good	0.0431	25
2	Aromatic hydrocarbons	0.5979	Poor	0.0324	11
3	Alcohols	0.5239	Poor	0.0290	22
4	Ketones	0.8614	Good	0.0342	23
5	Alkenes	0.5202	Poor	0.0380	11
6	Alkynes	0.9968	Good	0.0361	5
7	Ethers	0.7819	Good	0.0386	7
8	Esters	0.9559	Good	0.0377	15
9	Aldehydes	0.7210	Avg	0.0339	11
10	Chloro	0.7359	Avg	0.0380	7
11	Bromo	0.8337	Good	0.0319	7
12	Fluoro	0.8453	Good	0.0280	6
13	Nitriles	0.7773	Good	0.0350	6
14	Sulfurs	0.8979	Avg	0.0500	6
				0.5059	
	Average			0.0361±0.005	
			%R.S.D. = 13.84		
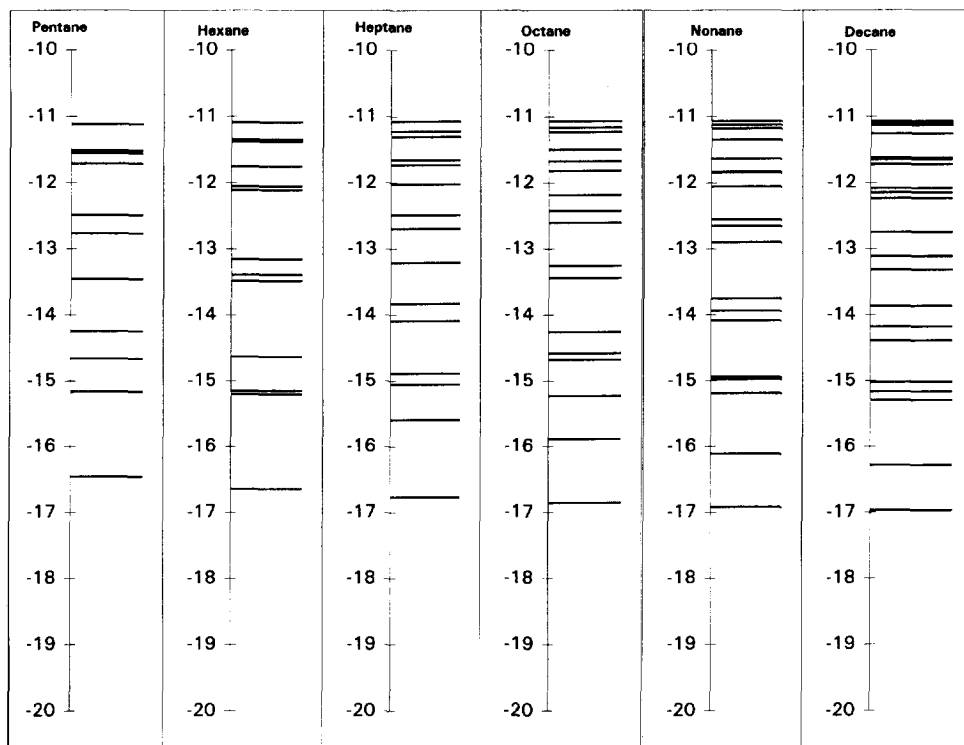
Fig. 5. Orbital diagram for C_5–C_{10} saturated hydrocarbons.

In a previous study of the PDHID [2] it was noted that the response on a per gram basis was approximately constant for the C_1–C_{10} normal hydrocarbons. This is similar to that for the FID where the response is approximately a function of the number of carbon atoms. For molecules which do not contain carbon, the FID response is lowered since the other atoms such as O, N, F, Cl, S do not ionize in the flame. Nevertheless, the response is frequently assumed to be constant in order to obtain an approximate concentration of an unknown compound. For precise work the FID response must be calibrated for each compound and the calibration factors included in the calculation of the concentration.

A similar situation exists for the PDHID in that it is a universal detector and if the response on a per gram basis were assumed to be constant, an approximate concentration of an unknown compound could be calculated, analogous to that done with the FID. These concentrations are often given in chromatographic data reduction procedures as a chromatographic percentage. For this reason we have ex-

amined in this study the response per gram for a large variety of compounds, containing various functional groups and heteroatoms. In principle the PDHID response per gram may be more constant than that of the FID since heteroatoms will show some response to the photoionization process. However, for precise work the PDHID would have to be calibrated for each compound. In analyzing the data in Table 2 we will examine the variations in the response per gram for compounds in various classes. This will give the analyst some idea of the error involved in assuming a constant response per gram.

Table 2 contains the data for each of the individual compounds included in this study. This consists of 174 compounds in various classes. In order to simplify the analysis we have summarized the results for each class in Table 3. Of principal interest are the average or mean of the response per gram, the range of the responses per gram, the standard deviation of the response per gram and the percent standard deviation for each class of compounds. This will reveal the variation in response per
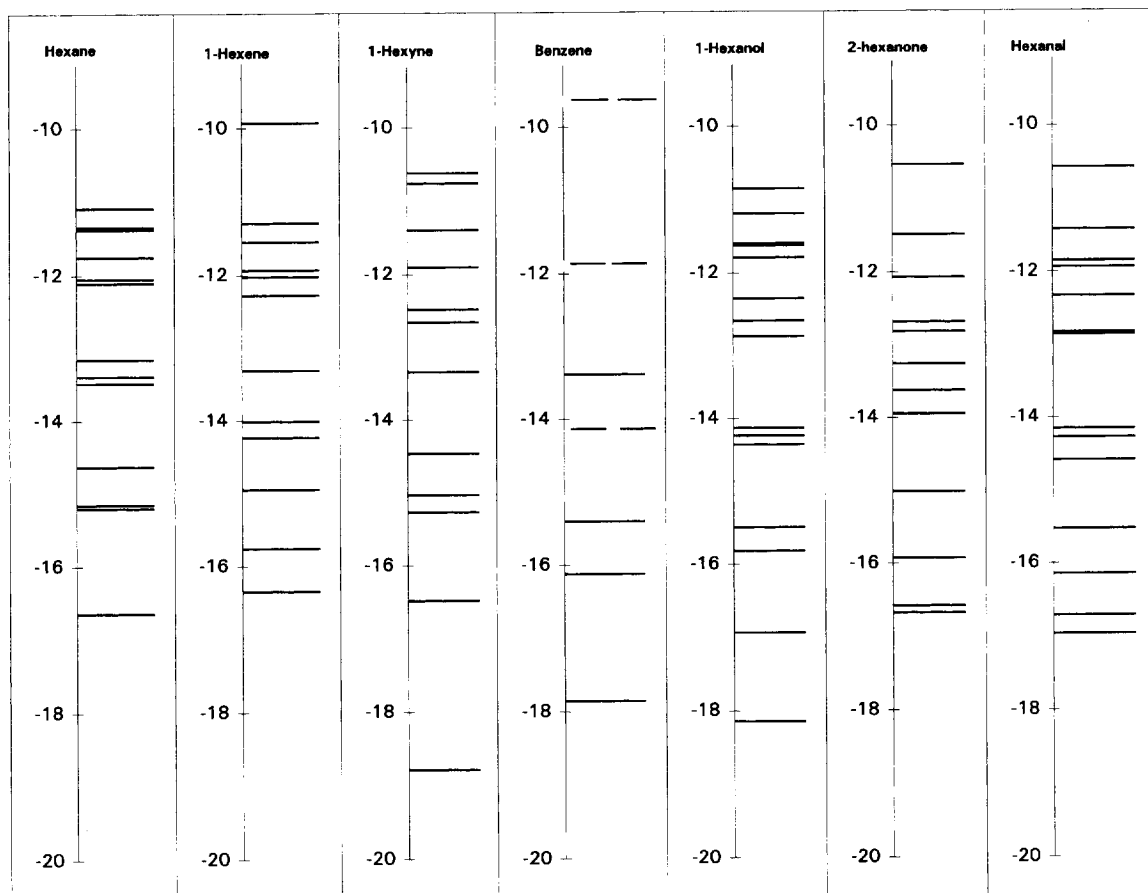
Fig. 6. Orbital diagram for C_6 unsaturated hydrocarbons, alcohols, ketones and aldehydes.

gram within a class and also the variation of the average responses between classes. The actual relative standard deviations are for the area ratios but since the errors in the weight ratio is small, the value will be applicable to the relative response factors.

For all saturated and cyclic hydrocarbons the range of relative responses per gram is from 0.72–1.18. The mean of these relative responses per gram is 0.946. This is close to one as expected since the relative response per gram is referenced to hexane, a saturated hydrocarbon. The standard deviation in each of the sub-classes of the saturated hydrocarbons varies only slightly and the overall variation in the saturated and cyclic hydrocarbons is 11%. This percent standard deviation is generally lower than that for the other classes of compounds. As can be seen in the last column of Table 3, the percent

standard deviation for some classes is as large as $\approx 40\%$, but the average is $\approx 20\%$. If an analysis were restricted to compounds in any of these classes, the percent standard deviation gives a measure of the error that might be expected by using the same response factors for all compounds in the mixture. However, in most analyses there are compounds from more than one class.

The mean of the responses on a gram basis varies for the different classes of compounds. It ranges from 0.53 to 0.95 for the various classes of compounds exclusive of the halogens. The average response of all compounds from all classes is 0.647. Thus the range from this mean for all classes of compounds exclusive of the halogens is -18% to $+40\%$. This gives the analyst some idea of the error that might be expected when the mixture contains
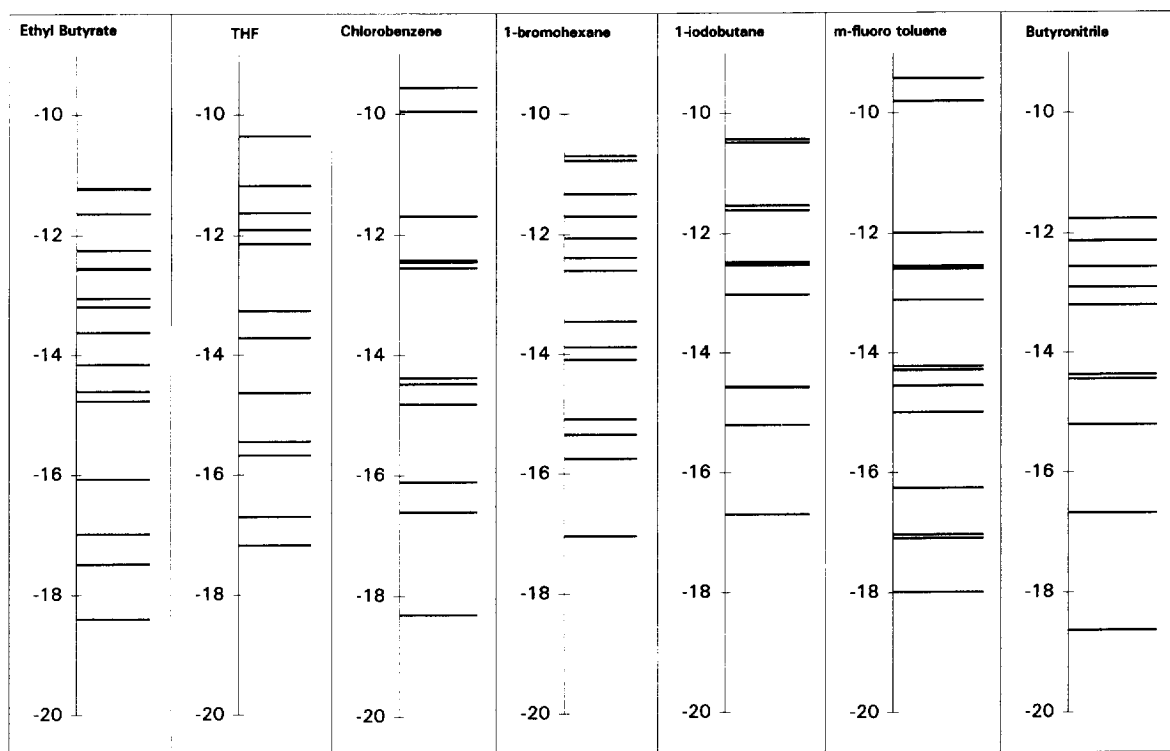
Fig. 7. Orbital diagram for ester, ether, halogen and nitrile compounds.

various classes of compounds and the detector is uncalibrated.

3.2. Rationale for response factors

Assuming that the bulk of the radiation from the He_2 continuum peaks at 14 eV and tails off to 17 eV, electrons lying in orbitals which are above -14 eV energy will be completely ionizable and only those orbitals are considered. Those below -14 eV will be only partially ionizable and are not considered initially. On this basis, a simple discussion of the orbital diagrams can be presented. The more precise determination of the ionizable electrons will be used in the quantitative correlation.

Figs. 5–7 represent the molecular orbital diagrams of molecules from various classes of compounds. These orbital diagrams are shown in order to provide a qualitative rationale for the various responses that were obtained experimentally. The values of the energies of these orbitals were obtained

from the AM1 method in HyperChem as noted earlier and then integrated into the Excel program for further data analysis.

Fig. 5 represents the orbitals for the normal alkanes, pentane to decane. Only the filled orbitals are considered and the orbital energies that are shown range from -10 eV to -20 eV although the energies go as low as -37 eV. From Fig. 5, the ionization potential decreases gradually but the number of orbitals increase dramatically from pentane to decane. Actually the ionization potentials from octane to decane are essentially constant. Since the number of orbitals increases as one goes from pentane to decane, the number of ionizable electrons increases and the response should not be dependent on the ionization potential. As shown experimentally the response does increase as we go from pentane to decane which proves that the response is dependent on the number of ionizable electrons and to a lesser extent on the ionization potential.

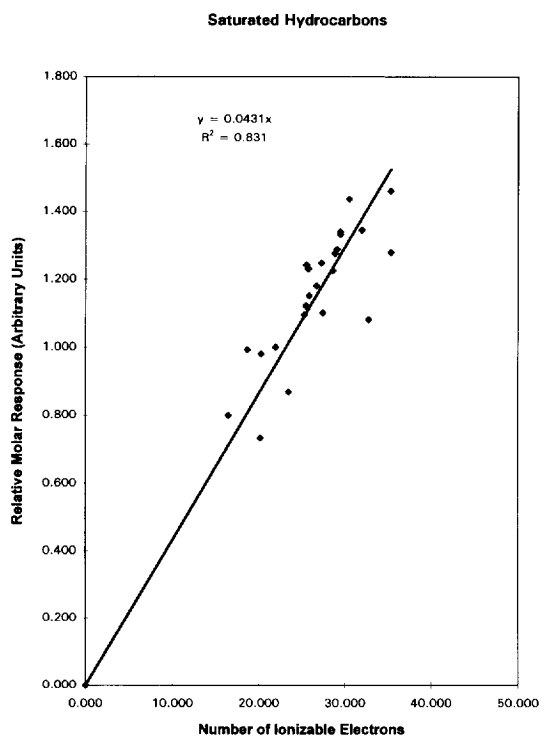In Fig. 6, the orbitals of various compounds from

Saturated Hydrocarbons

Fig. 8. Response/mol versus number of ionizable electrons from He$_2$ continuum: saturated hydrocarbons.
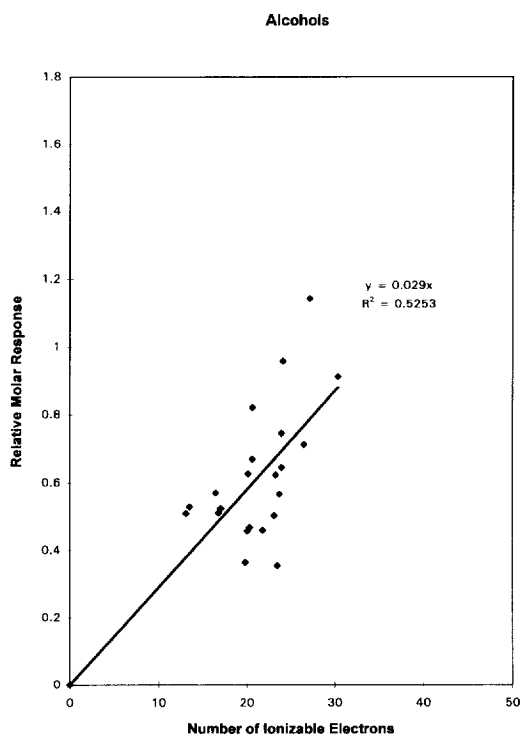
Alcohols

Fig. 9. Response/mol versus number of ionizable electrons from He$_2$ continuum: alcohols.

different classes of compounds are shown. In order to maintain uniformity the compounds selected are such that each of them have six carbon atoms. The ionization potential of 1-hexene is 9.92 eV which is lower than that of hexane which has an ionization potential of 11.08 eV. However the number of orbitals above -14 eV and hence the number of ionizable electrons is greater for hexane than 1-hexene. This is in agreement with the observed greater response for hexane than 1-hexene. Again, the detector response is influenced more by the number of ionizable electrons than the ionization potential. A comparison with the orbitals of benzene further proves this point. Benzene has a response of 0.66 relative to hexane or nearly 1/2 of the response of hexane. Benzene has five orbitals above -14 eV and hexane has nine orbitals. This is a ratio of 0.56 which correlates well with the relative response for hexane and benzene. 1-Hexyne also has fewer orbitals than hexane above -14 eV which again contribute to a reduced response compared to hexane. Even

though 1-hexene and 1-hexyne have the same number of orbitals above -14 eV, the response for 1-hexene is greater than 1-hexyne. This may be due to the fact that the photoionization cross sections for ionization of the electrons in 1-hexene and 1-hexyne are different in opposition to the major assumption of constant cross sections.

Fig. 7 also presents the orbitals from various classes of compounds such as esters, ethers, halo compounds and nitriles. The esters have the same number of ionizable electrons above -14 eV and should theoretically have the same response as hexane. Experimentally ethyl butyrate has nearly the same response as hexane. Also the presence of an ester group tends to increase the ionization potential as compared to hexane. The ether has a lower ionization potential than hexane. It also has four fewer ionizable electrons than hexane but it exhibits an unusually low response which is nearly half that of hexane. Experimentally, cyclic compounds exhibit low responses which might be due to the delocaliza-
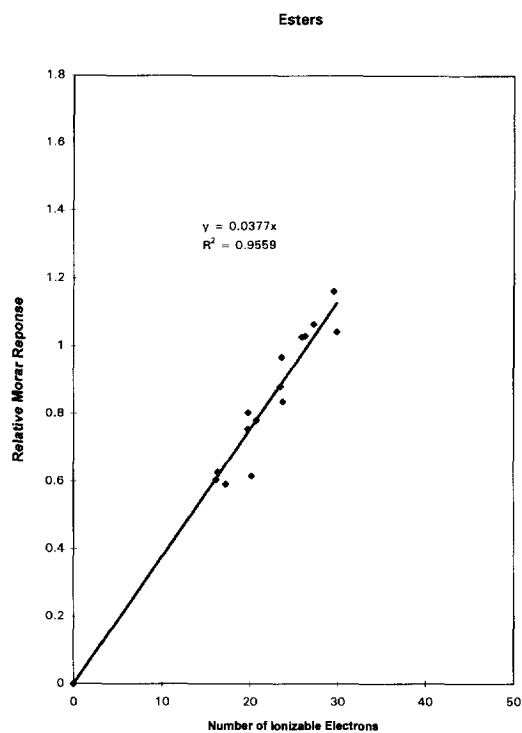
Esters

Fig. 10. Response/mol versus number of ionizable electrons from He$_2$ continuum: esters.
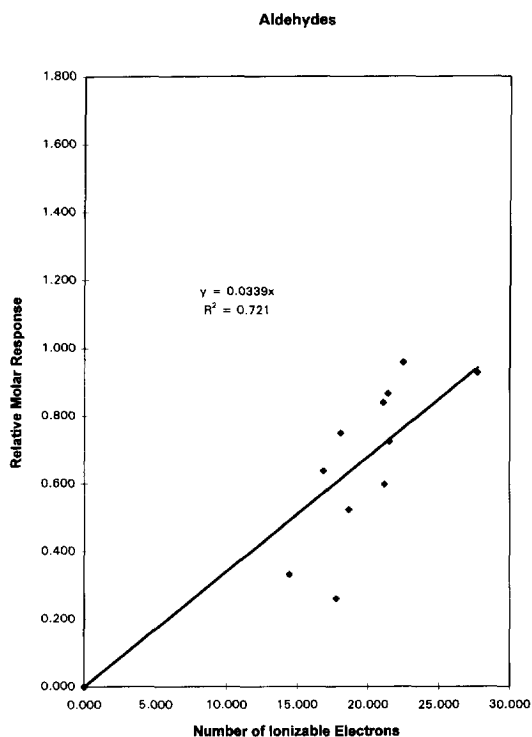
Aldehydes

Fig. 11. Response/mol versus number of ionizable electrons from He$_2$ continuum: aldehydes.

tion of electrons in them. The nitrile group tends to lower the energy of the high lying orbitals. The ionization potential for butyronitrile is higher than hexane. Further there are half as many orbitals above −14 eV in comparison to hexane and butyronitrile exhibits a response which is half that of hexane.

Above −14 eV hexanal has four ionizable electrons less than hexane and rightfully exhibits a decreased response compared to hexane which once again shows that the response is dependent on the number of ionizable electrons. 1-Hexanol and 2-hexanone have two ionizable electrons less than hexane however their responses are much lower than that of hexane

The response of both the chloro and fluoro compounds are more comparable to benzene than hexane. When comparing them to benzene the presence of the chloro and fluoro substitutents also tend to raise the energy of the high lying orbitals thus lowering the ionization potential though to a much less extent in comparison to hexane. Chlorobenzene

has nearly the same response as benzene which is due to the fact that above −14 eV, chlorobenzene has nearly the same number of orbitals and hence the same number of ionizable electrons as benzene. Both chlorobenzene and m-fluorotoluene have the same number of orbitals above −14 eV but m-fluorotoluene has a lower response experimentally than chlorobenzene.

1-Bromohexane has nearly the same number of orbitals as hexane above −14 eV and hence the response is directly dependent on the number of ionizable electrons. The same conclusion can be drawn for the iodo compounds in particular 1-iodobutane which has seven orbitals above −14 eV which is less than the number of orbitals in hexane and it rightfully exhibits a lower response than hexane. The iodo and bromo substitutents tend to lower the ionization potentials in comparison to hexane.

Although not much of a differentiation can be made for various molecules using helium, they can

be differentiated if the helium is doped with 5% Kr [3]. By doping helium with Kr the emission spectra of Kr is obtained which consists of resonance lines and the dimer continuum emission [4]. The two resonance lines are at 10.1 and 10.6 eV of which the resonance line at 10.1 eV is more intense while the Kr_2 continuum is at ~8.6 eV. Both benzene and 1-hexene have high lying orbitals i.e. low ionization potentials. Therefore they will be ionized by the 10.1 eV resonance line of Kr while 1-hexyne will be ionized only by the lower intensity 10.6 eV resonance line of Kr and hence will give a lower response than 1-hexene and benzene. Hexane should not give a response to Kr since the highest energy orbitals is − 11.08 eV. This is the subject of the following paper where the dependence of the Kr-doped PDPID response on the number of ionizable electrons is considered more quantitatively |9|.

3.3. Correlation of response with the number of ionizable electrons

Next we consider correlating the response of all the compounds from various classes with the number of ionizable electrons calculated considering the complete emission spectrum. Graphs of the relative responses versus the number of ionizable electrons have been prepared for all of the classes of compounds and these can be found in the original work [10]. Figs. 8–11 are plots of the responses for the saturated, hydrocarbons, alcohols, esters and aldehydes versus number of ionizable electrons. These classes are representative of all classes in that the saturated hydrocarbons and esters give a reasonably good correlation whereas the aldehydes give a good correlation and the alcohols give a poor correlation. The interpretation of the results is restricted to a straight line through the origin. Table 3 gives a summary of the slopes of the graphs for the various classes of compounds, the correlation coefficients, R^2, and a qualitative evaluation of the correlation.

Note that the slopes from the various classes are in reasonable agreement. The slope for the sulfur compounds is exceptionally high. We have no explanation for this behavior. The saturated and cyclic hydrocarbons also show a higher sensitivity than the other classes of compounds. The average slope from all 14 classes is 0.0361 with a percent standard

deviation of 13.8. Considering the accuracy of the theoretical calculations and the assumption that the photoionization cross-sections for all electrons are the same, the correlation is quite good. This is especially significant considering the wide variety of elements and functional groups considered.

4. Conclusions

The weight response factors for the classes of compounds varies from 0.53 to 0.95 for the various classes of compounds exclusive of the halogens. This could introduce an error of − 18% to + 40% of the magnitude based upon a constant response. The molar responses are correlated to the number of ionizable electrons in a molecule. Based upon this correlation we conclude that to a first approximation the response of the PDHID is a function of the number of ionizable electrons from the He_2 continuum. As we will see in a subsequent paper in this journal, more detailed evaluation using Kr doped photoionization requires adjustment of the parameters involved in the calculation [9].

In the calculations reported in this paper all the parameters supplied in the HyperChem program were used.

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