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Double photoionisation spectra of small molecules and a new empirical rule for double ionisation energies

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Abstract

Complete double photoelectron spectra are presented for 18 small molecules where the location of charges in the cations and dications is relatively clearly defined. The data demonstrate the importance of a coulombic repulsion contribution to the double ionisation energies. Examination of data for a wide range of molecules leads to a new empirical rule to calculate double ionisation energies from the molecules' single ionisation energies and maximum dimensions. Where single and double ionisation energies are known the rule allows the deduction of plausible intercharge distances.

Keywords: Double photoionisation; Double ionisation energies; Iodides; Diiodides; Dibromides; Diamines; PEPECO

1. Introduction

A "rule of thumb", stating that the double ionisation energy (DIE) of an atom or molecule is approximately 2.8 ± 0.1 times its first single ionisation energy (IE), was suggested many years ago [1]. It is obeyed roughly by atoms as diverse as Ba and Ar, and by many molecules, and so has been found useful in planning experiments on compounds whose double ionisation energies were unknown. The precise value of the factor has been reconsidered several times while retaining the form of the rule; for example for aromatic hydrocarbons, in the light of new double ionisation energies, a factor of 2.65 was found appropriate [2]. Accurate double ionisation energies have recently been measured for many more compounds, and have revealed some strikingly large deviations from the rule. For SF_6 and also for CCl_4 the ratio DIE/IE is only 2.45, while for pyrrole it is 2.93. Two possibly related anomalies were noticed in a recent double photoionisation study of HI, CH_3I and CF_3I [3]. Firstly, while the single ionisation energy increases on going from HI to CF_3I, the double ionisation energy decreases. Secondly, while the single ionisation spectra are all similar in form, in double photoionisation the spectrum changes drastically between HI and CH_3I, whose spectra are alike, and CF_3I, whose spectrum is quite different. It was suggested that the difference might arise from a change between localisation of both charges on the iodine atom in HI^{2+} and CH_3I^{2+} to a wider charge separation in the fluorinated dication.

To investigate these matters more fully, we have measured double photoionisation spectra of a number of iodides and diiodides, dibromides, diamines and other compounds where the location of charges in the lowest states of the dications at the instant of their formation may be estimated with reasonable confidence. Because the geometry of the dications may change drastically thereafter, the analysis is concentrated on *vertical* ionisation energies. The variations in ionisation energies and in spectra fully confirm the expected importance of intercharge

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distance. After analysis of selected data we propose to represent double ionisation energies using a simple coulombic model, which proves superior for most classes of molecules and even atoms, to the old rule of thumb. The new model provides a clearer physical insight into double ionisation energies, in the spirit of Koopmans' theorem, than did the old rule, and even allows limited structural deductions from ionisation energies.

In this paper, we present double photoionisation spectra of ethyl-, *n*-propyl- and *n*-hexyl iodides, diiodomethane, 1,2-diiodoethane and 1,3-diiodopropane, dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobenzene, *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine (TMMD), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED), *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine (TMPrD) and *N*,*N*,*N*′,*N*′-tetramethyl *p*-phenylenediamine (TMPhD), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,4-dithiane and dimethoxymethane. The spectra have been measured by the time-of-flight photoelectron–photoelectron coincidence (TOF-PEPECO) technique, which provides complete energy information on the emitted electrons with no discrimination by electron energy or emission angle.

2. Experimental

The TOF-PEPECO technique has been described both in its original form [4] and with the most recent developments [3,5]. Briefly, ionisation is by 5–10 ns pulses of vacuum ultraviolet light from an atomic discharge in He, selected in wavelength by a toroidal grating monochromator. Photoelectrons of all energies are forced by the inhomogeneous field of a conical permanent magnet to follow the field lines of a 5.5 m solenoid to a distant detector, where their arrival times are registered. A multi-hit time-to-digital converter records all electron arrival times after each pulse and the flight times can then be converted to energies using a direct two-parameter calibration. Measurements of the known photoelectron spectrum of oxygen at 21.22 eV are done before and after each run on a new compound to establish the calibration parameters. If surface potential changes have caused calibration drift in a run, the data can be divided into blocks in time sequence. Individual data blocks are then calibrated separately using an autocorrelation algorithm to put all on a common scale.

The compounds used in this study were all obtained commercially. Their purity was established before the double ionisation runs by comparison of their photoelectron spectra at 21.22 eV photon energy with literature spectra.

3. Results and discussion

The compounds have been grouped for graphical presentation in five series: monoiodides, diiodides, dibromides, diamines and other compounds. Double ionisation spectra for these series of molecules are shown respectively in Figs. 2–6. Numerical data for these and other compounds are listed in Tables 1 and 2; as the ionisation energies are mostly from work in this laboratory, references are given only where single ionisation potentials have been taken from other sources [6–18] or where detailed double ionisation spectra have been published [19–22].

The single ionisation spectra of the monoiodides (Fig. 1) clearly demonstrate that charge is located on the iodine atoms in the ground states of all the monocations, because the lowest bands all show the characteristic spin–orbit splitting of iodine. Of the double photoionisation spectra, on the other hand, only that of methyl iodide shows the double charge located mainly on the iodine atom. In spectra of the larger molecules the characteristic spin–orbit

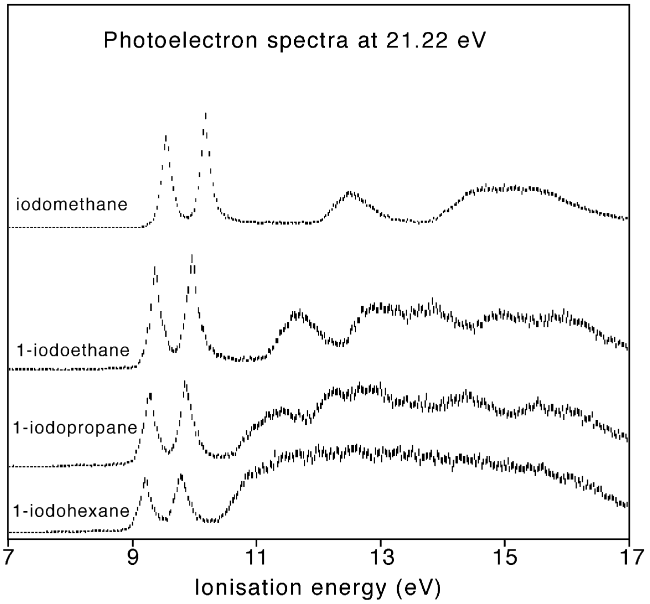

Fig. 1. Single photoionisation spectra of the monoiodide series of compounds.

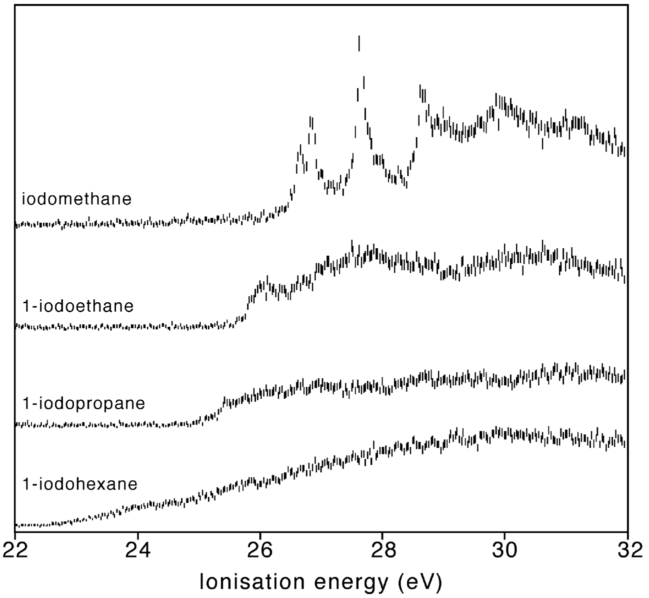

Fig. 2. Double photoionisation spectra of the monoiodides.

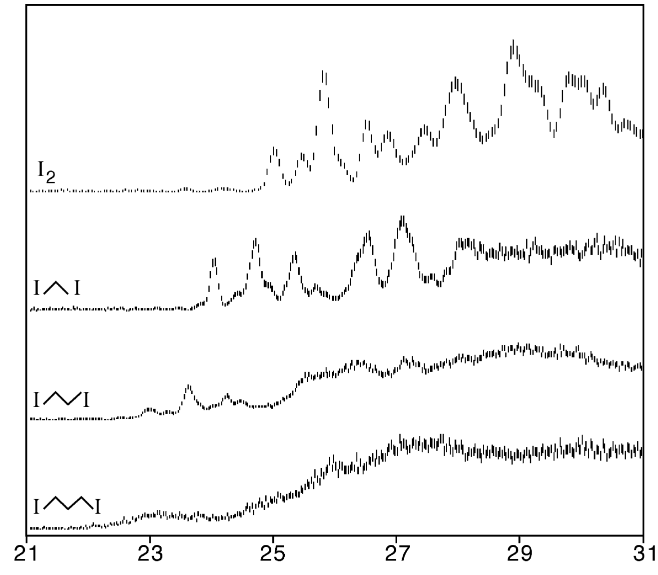

Fig. 3. Complete double photoionisation spectra of the diiodide series of compounds.

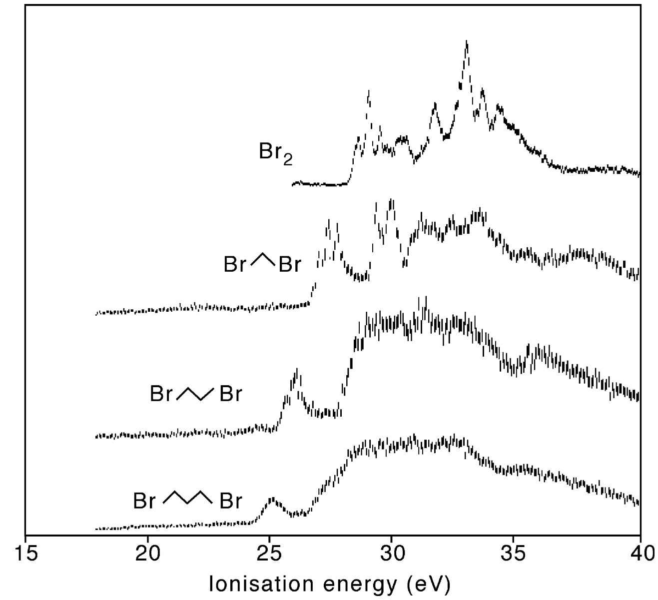

Fig. 4. Complete double photoionisation spectra of the dibromide series of compounds taken with He (IIα) light.

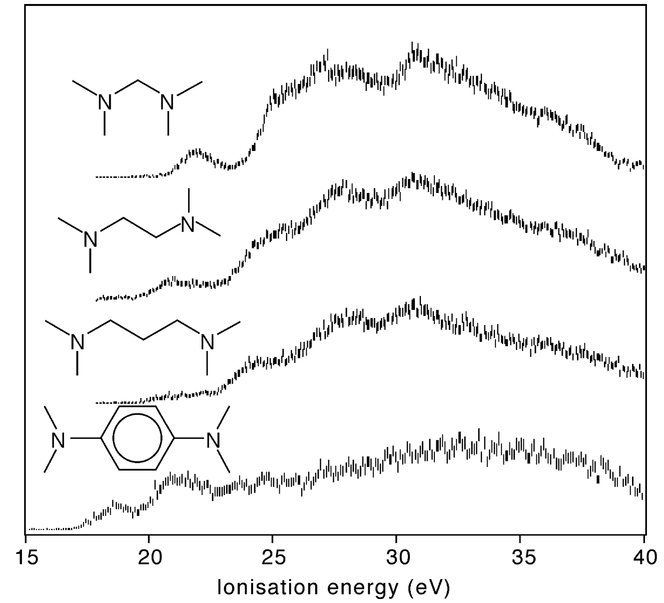

Fig. 5. Complete double photoionisation spectra of the diamine series of compounds taken with He (IIα) light.

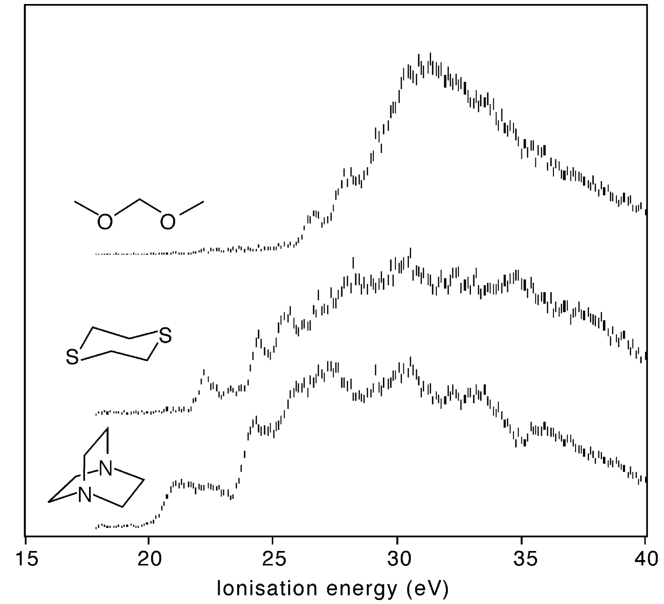

Fig. 6. Complete double photoionisation spectra of DABCO, 1,4-dithiane and dimethoxymethane taken with He (IIα) light.

splitting disappears, suggesting that at least one charge must be on the carbon moiety even in the ground states of the dications. In double ionisation spectra of the diiodides, by contrast, characteristic spin–orbit splitting, indicating charge location on iodine atoms, persists certainly to the 1,2 C_2 and probably to the 1,3 C_3 compound. There is also a striking breakdown of the old rule, as the IE of methylene iodide is higher than that of diatomic iodine, but this order is reversed in the dications. As the chain length of the diiodide molecules is increased the IE decreases only slightly, but there is a rapid fall in DIE. The same behaviour is shown by the monoiodides, the dibromides and somewhat less dramatically, by the diamines. These qualitative observations all suggest that the distance r_{12} between two charges in the dications is a major factor determining the DIE. From the standpoint of the old rule, we can examine the ratios DIE/IE for related compounds of increasing size. For the diiodides the trend is clear: I_2, 2.63; ICH_2I, 2.59; $I(CH_2)_2I$, 2.50: $I(CH_2)_3I$, 2.45. (Here we have taken the centre of each multiplet caused by spin–orbit splitting, so as to concentrate on purely orbital effects). A similar pattern is found in the

Table 1
Ionisation and distance data for molecules where intercharge distances in the dications can be estimated from atom positions

Compound	IE (eV)	DIE (eV)	r_{12} (pm)	r_{12} (calc.)	Refs.
H_2	15.9	51.4	74	71	
N_2	15.58	43.0	110	133	[19]
O_2	12.1	36.4	121	119	[19]
CO	14.0	41.5	113	108	[20]
I_2	9.31	24.95	267	258	[21]
Br_2	10.56	28.4	228	220	
Cl_2	11.48	32.6	199	158	
CS_2	10.1	27.0	310	243	[19]
CO_2	13.79	37.3	232	167	[22]
ICH_2I	9.46	24.0	371	364	
$I(CH_2)_2I$	9.56	22.95	516	605	
$I(CH_2)_3I$	9.38	22.5	(622)	617	
$BrCH_2Br$	10.61	27.0	326	317	[7]
$Br(CH_2)_2Br$	10.59	26.0	468	429	[6]
$Br(CH_2)_3Br$	10.35	25.0	(578)	417	[8]
SF_6	15.5	37.5	320	341	[9]
CF_4	16	40	217	242	[10]
CCl_4	11.69	28.5	293	417	[11]
CBr_4	10.39	26	319	369	[12]
DABCO[a]	7.52	21.03	258	259	[13]
1:4-dithiane	8.58	22.18	353	351	[14]
$(MeO)_2CH_2$	10.42	26.6	222	315	[15]
TMMD[b]	7.74	21.89	249	239	[16]
TMED[c]	7.61	20.90	383	279	[16]
TMPrD[d]	7.84	21.01	507	308	[17]
TMPhD[e]	6.84	17.37	569	500	[18]

Distances r_{12} in the fourth column are established values from spectroscopy or molecular structure calculations, while those in the fifth column are estimated from the ionisation energies using Eq. (3).

[a] Diazabicyclo222-octane.

[b] *NN′*-tetramethyl methylene diamine.

[c] *NN′*-tetramethyl ethylene diamine.

[d] *NN′*-tetramethyl,1:3-propylene diamine.

[e] *NN′*-tetramethyl *p*-phenylene diamine.

Table 2
Vertical ionisation energies and distance data for other compounds

Compound	IE (eV)	DIE (eV)	Est. r_{12} (pm)	Calc. r_{12}
Trans-Butadiene	9.09	25.0	380	232
Cyanogen	13.37	35.2	360	200
Pyrrole	8.2	24	230	195
Furan	8.9	25.5	226	196
Benzene	9.25	25	280	249
Pyridine	9.7	25.5	280	279
Naphthalene	8.15	22	500	285
Azulene	7.42	20.45	500	281
Quinoline	8.67	23	500	295
Biphenyl	8.5	21.5	710	414
Anthracene	7.46	19.6	720	364
Phenanthrene	7.9	20.6	700	360
Pyrene	7.44	19.8	710	338
Tetracene	6.96	18.6	960	353
Perylene	6.85	18.0	750	396
Pentacene	6.61	17.4	1200	406
Coronene	7.20	18.7	840	406
C_{60}	7.6	19.5	1200	417
Fe $(CO)_5$	8.8	24.3	600	235
COT (C_8H_8)	8.5	22.5	350	305
Iodomethane	9.54	26.66	214	203
1-Iodoethane	9.39	26.0	280	215
1-Iodopropane	9.28	25.2		240
1-Iodohexane	9.22	23.3		381
N_2O	12.89	35.8	230	155
OCS	11.19	30.5	272	196
SO_2	12.5	34.3	256	169
C_2H_2	11.40	32.2	112	162

Ionisation data for compounds named in italics are from Tobita et al. [2] and may be adiabatic rather than vertical values. The distances in the fourth column are maximum separations of heavy atoms, many estimated from standard bond lengths and angles.

dibromides: Br_2, 2.70; $BrCH_2Br$, 2.58; $Br(CH_2)_2Br$, 2.46: $Br(CH_2)_3Br$, 2.48. The same trend with increasing size is found in the ratios for the monoiodides and for other groups of compounds where reliable double ionisation energies are known, for instance benzene, 2.67; naphthalene, 2.61; coronene, 2.57, fullerene 2.50. There can be no doubt that size matters.

To quantify the effect, we next examine pairs of molecules where the charges in the dications are clearly on identical atoms, the first ionisation energies are only slightly different, but the charge-bearing atoms are at different distances apart in the neutral molecules. The coulomb energy, $e^2/4\pi\varepsilon_0\varepsilon_r r_{12}$, should contribute the dominant part of any difference in double ionisation energy between members of such pairs. By comparing differences in calculated coulomb energy (with the relative permittivity ε_r as 1.0) against differences in DIE we may cancel some errors in estimating the absolute intercharge distances. The calculated and experimental DIE differences for pairs that fit the above criteria are generally in good agreement, for instance ICH_2I and ICH_2CH_2I, $\Delta DIE_{obs} = 1.0 \pm 0.05$ eV, $\Delta DIE_{calc} = 1.09$ eV; $BrCH_2Br$ and $BrCH_2CH_2Br$, $\Delta DIE_{obs} = 1.32 \pm 0.05$ eV, $\Delta DIE_{calc} = 1.34$ eV, SF_6 and CF_4 $\Delta DIE_{obs} = 2.0 \pm 0.2$ eV, $\Delta DIE_{calc} = 2.14$ eV.

Because we expect that orbital energies, reflected in ionisation energies will be reflected also in double ionisation energies, we also tried to find pairs of molecules whose structures imply similar charge localisation but whose first ionisation energies differ. Comparison between differences in DIE and differences in IE for such molecules could reveal the parts of any relationship independent of the coulomb energy. Unfortunately, the data for the few available pairs of this sort (benzene/pyridine, pyrrole/furan, naphthalene/quinoline/azulene, CO_2/N_2O) show only that any non-coulomb part of the DIE difference is about twice the IE difference (factor 2 ± 0.25).

The simplest model for double ionisation energies, based on Koopmans' theorem and consistent with the observations above would be:

$$\mathrm{DIE} = 2 \times \mathrm{IE} + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r_{12}} \tag{1}$$

To test this model we select molecules from our new and recently published data, to meet strict criteria. The spectra must show that both electrons removed in forming the dicationic ground state come from the same orbital as the one electron removed in single ionisation, or from equivalent orbitals. To achieve this the orbital(s) must be predominantly localised on identical atoms, and we further require that their distance apart in space be known or capable of reliable estimation. Application of these criteria leads to a preliminary list of molecules, for which we show vertical single and double ionisation energies and interatom distances in Table 1. Of the newly measured compounds, 1,3 dibromopropane is still omitted at this stage because its spectra suggest a mixture of conformers in the gas phase, making the distance estimate unreliable. The tetramethyl diamines and dimethoxymethane are also omitted, because of uncertainty over the extent of charge distribution onto the methyl moieties. For some of the remaining molecules, distances between the atoms bearing the final charges are taken from known gas phase structures, mainly from spectroscopic or electron diffraction data. Where these are not available the distances have been estimated theoretically, by complete geometry optimisations using estimated structures as input data to a standard molecular structure program package. Becke's three parameter fit was used with the correlation functional of Lee, Yang and Parr (B3LYP), as implemented in the Gaussian 03 package [23].

A first test of the coulombic model (1) was carried out on these selected data. A rather close linear relationship was found between (DIE – 2 × IE) and $1/r_{12}$, shown in Fig. 7, with a slope of 16 eV Å when forced to intersect the origin. The standard deviation of double ionisation energies calculated using this model is 0.64 eV, significantly better than the old rule of thumb with the widely-used factor of 2.7 ($\mathrm{DIE} = 2.7\mathrm{IE}$, $\sigma = 2.2$ eV) or even the old rule with a factor optimised for these specific data ($\mathrm{DIE} = 2.54 \times \mathrm{IE}$, $\sigma = 1.3$ eV). This seems to be a clear sign of superiority of the coulombic model. The steep slope of Fig. 7 is disconcerting, however, since even if the relative permittivity of molecules is the same as that of free space, the slope should be 14.4 eV Å, and for a realistically higher permittivity the slope should be lower. When the fit is unconstrained, the best line relating DIE – 2IE to $1/r_{12}$ has a lower slope and does not pass through the origin, but implies a constant added term, which seems unphysical. A better fit is obtained to the equation of the form:

$$\mathrm{DIE} = k \times \mathrm{IE} + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r_{12}} = k \times \mathrm{IE} + \frac{g}{r_{12}}. \qquad (2)$$

This extension of the old rule of thumb, with a scaled coulomb term, is closely related to the model used by Hampe et al. for dianions [24]; it fits our selected data significantly better than the old rule. The parameters are first estimated from a linear least-squares fit of $r_{12} \times \mathrm{DIE}$ against $r_{12} \times \mathrm{IE}$, giving gradient k and intercept on the ordinate g (Fig. 8). Parameters minimising the error in double ionisation energies in Eq. (2) were then found by a grid search, with those k and g values as a starting point. The most effective equation for the ionisation energies of these selected molecules was found to be

$$\mathrm{DIE} = (2.20 \pm .03)\mathrm{IE} + (11.5 \pm 1)/r_{12} \qquad (3)$$

with energies in eV and distances in Angstrom units. The standard deviation is reduced to 0.4 eV.

To test the usefulness of this form of equation further, we have applied it to a wide range of species ranging from closed-shell atoms, diatomic and triatomic molecules up to molecules as large as the C_{60} fullerene. The ionisation energies not conveniently tabulated elsewhere, many from our own unpublished results, are presented in Tables 1 and 2. For consistency, the lowest *vertical* ionisation energies are used wherever possible. Intercharge distances have been crudely estimated in some cases by simple geometric addition of standard bond lengths to find the furthest possible separation of atoms other than H in the ground state molecular structures. For all the compounds we also list

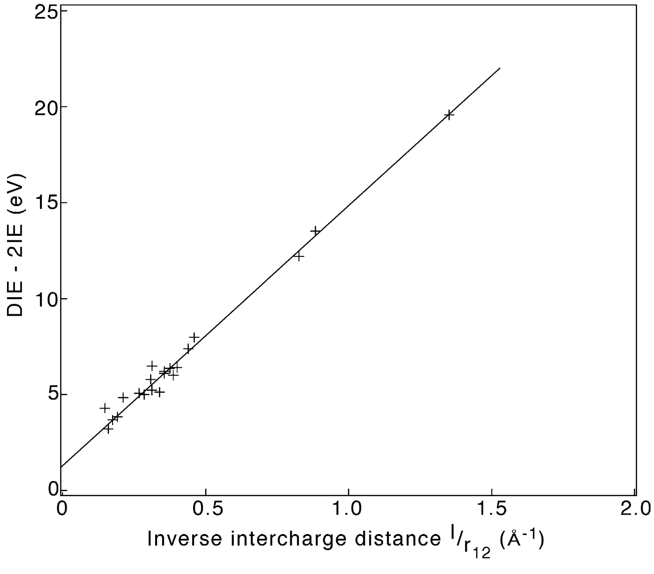

Fig. 7. Plot of (DIE – 2IE) against reciprocal distance for compounds selected from Table 1, as explained in the text.

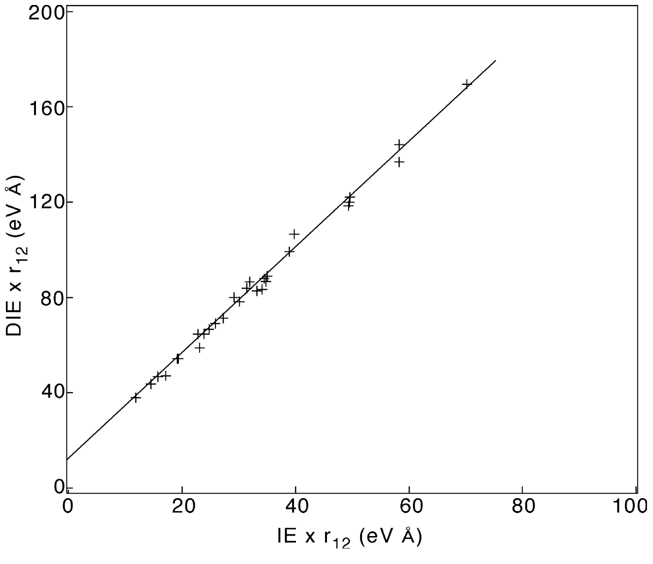

Fig. 8. Plot of $r_{12} \times \mathrm{DIE}$ against $r_{12} \times \mathrm{IE}$ for all the molecules listed in Table 1. The line has slope 2.175 and intercept 11.6 eV Å.

the apparent intercharge distances derived from the known single and double ionisation energies by inverting Eq. (3).

Examination of the tables shows generally good agreement between the intercharge distances estimated reliably (Table 1) and the distances which fit Eq. (3). Even for closed-shell atoms (not listed), Eq. (3) gives remarkably good predictions of double ionisation energies if the intercharge distance is set to 1.3 times the atomic radius [25]. The triatomics CO_2, OCS and CS_2 are surprising exceptions, with apparent intercharge distances less than the spacing of the outer atoms from which the electrons are indubitably removed. For the conjugated and aromatic compounds too (Table 2), the intercharge distances that fit the equation are always less than the separation in space of the most distant heavy atoms. This may be understood as a result of delocalisation, but a quantitative analysis has not been attempted.

The values of the parameters, $k = 2.2\,\text{eV}$ and $g = 11.5\,\text{eV}\,\text{Å}$ may also bear discussion. The deviation of k from 2.0 can be interpreted as an expression of the "reorganisation energy", as it affects double ionisation. In the early days of photoelectron spectroscopy it was noted that single ionisation energies are about 10% lower than SCF orbital energies interpreted by Koopmans' theorem [26], mainly because of orbital relaxation in the ions. The remaining electrons may thus be seen as more strongly bound than those in the neutral molecule, increasing the second ionisation energy. The reduction of g from the free-space value of $14.4\,\text{eV}\,\text{Å}$ can be reformulated as a mean molecular relative permittivity of 1.25. More profound theory would be needed to judge whether these values are reasonable, but in view of the empirical nature of this correlation we question whether such a theoretical effort is justified. In formation of the excited states of dications, both the orbital energies and the charge localisation are presumably different from those involved in forming the ground state, so extension of the present model to such states seems problematic.

4. Conclusions

Incorporation of coulomb repulsion energy in a modified form of the old rule of thumb clearly explains and removes some outstanding discrepancies which arose from the assumption of a fixed final charge separation. It is certainly possible to predict double ionisation energies from single ionisation energies more accurately using Eq. (3) than by the old rule, provided one knows the likely distance between the final charges. As this knowledge is most often lacking, however, the formula may not be of great practical use in this sense. It may possibly be useful as a guide to molecular conformation of some flexible molecules.

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